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THE JOURNAL OF SOIL SCIENCE

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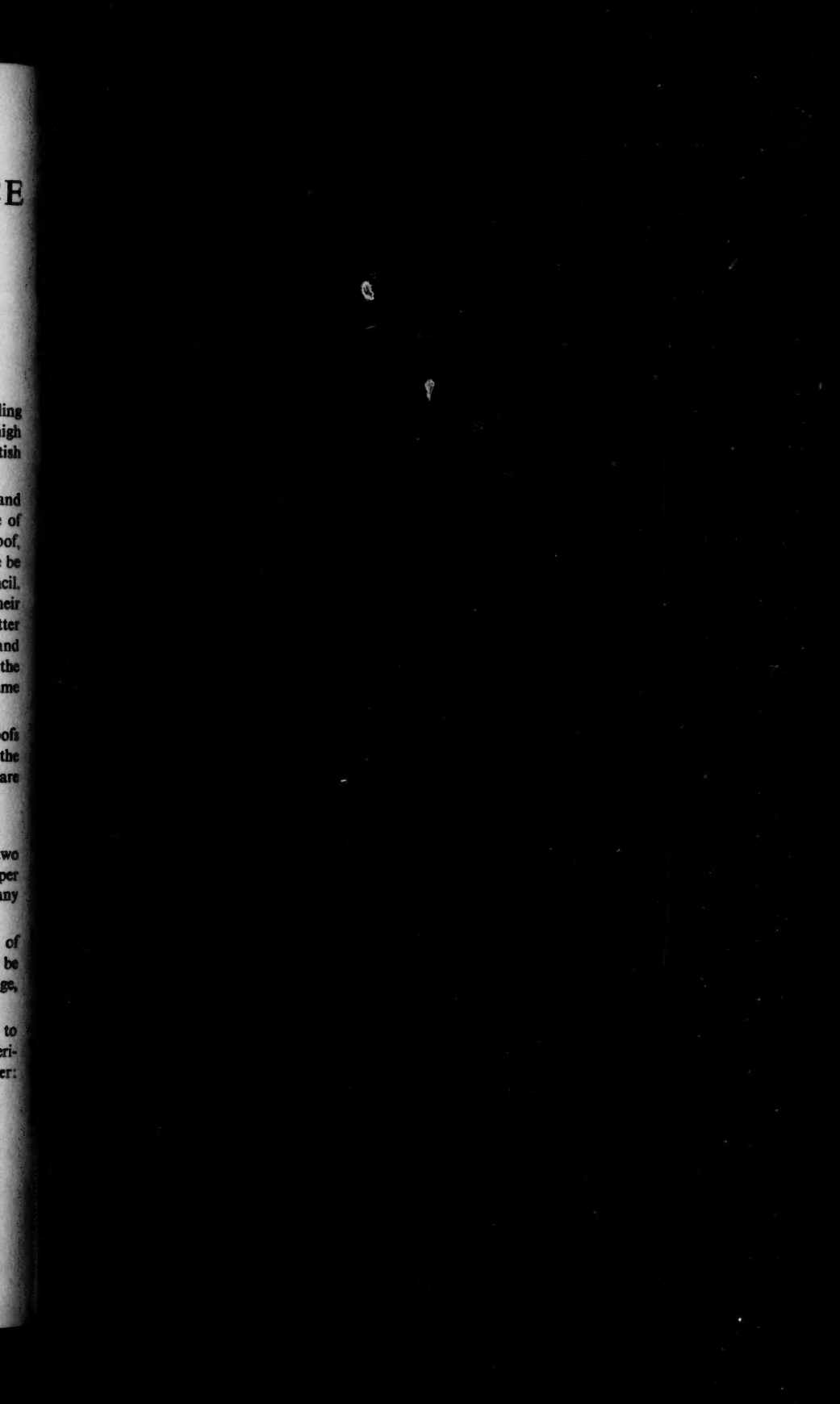

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THE EFFECT OF ELECTROLYTE CONCENTRATION ON SOIL PERMEABILITY

J. P. QUIRK[1] AND R. K. SCHOFIELD
(Physics Department, Rothamsted Experimental Station)

SEVERAL Californian workers have investigated the effect of electrolyte concentration on soil permeability, e.g. Bodman and Fireman (1939, 1950), Fireman (1944), and Christiansen (1947). Christiansen (1947) was of the opinion that the use of water of very low electrolyte content could result in soil sealing to such an extent that reclamation of alkali soils would not be possible.

The work of Bodman and Fireman (1939, 1950) has shown that a satisfactory permeability can be maintained with a soil which is 30 per cent. saturated with sodium, by using a high concentration of electrolyte. They did not investigate the region between the initial high salt concentration and distilled water, the use of which resulted in a drastic reduction in permeability.

Fireman (1944) working with Hesperia sandy loam obtained a high and constant permeability when 800 p.p.m. $CaCl_2$ solution ($7{\cdot}3 \times 10^{-3}$ M) was used as the percolating liquid. When distilled water was used the permeability decreased in a period of 5 hours to less than one-hundredth of that obtained with the $CaCl_2$ solution. A NaCl solution containing 4,500 p.p.m. ($7{\cdot}7 \times 10^{-2}$ M) with this soil caused a continuous decrease in permeability, but for the period of the experiment the rate of flow was always higher than that obtained with distilled water. For a bed of fine aggregates (95–300 microns) of Yolo clay loam Greacen (1949) found that the permeability remained relatively constant for $CaCl_2$ concentrations greater than 60 p.p.m. ($5{\cdot}5 \times 10^{-4}$ M) while 6,000 p.p.m. NaCl ($1{\cdot}02 \times 10^{-1}$ M) were required for the concentration to have any effect in maintaining the permeability.

Despite the obvious effect of electrolyte on soil permeability the main emphasis has been given to the exchangeable sodium percentage and conductivity of the irrigation water as an index of the degree to which sodium will occupy exchange positions on the clay surface. Soils in arid and semi-arid regions often have high exchangeable sodium percentages before being irrigated and for this reason the quantity of electrolyte in the irrigation water should be given greater consideration. However, the results required, to establish criteria for the level of electrolyte needed to maintain a satisfactory permeability of soils saturated to varying degrees with sodium, are not available.

Kelley (1950) states 'where high-Na^+ irrigation water is applied the soil usually remains fairly permeable to that water despite the undesirable adsorption of Na^+ by base exchange, because of the flocculating effect of the salts of the water; but when an irrigation water of much lower concentration is substituted markedly reduced permeability

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soon manifests itself'. This point of view is in accord with the laboratory work of Bodman and Fireman (1939).

Description of the Soil

The soil used in this investigation was obtained from the surface 3 in. of Sawyers 1, a field on the Rothamsted Farm. This soil was chosen as it is non-calcareous. The mechanical analysis of the soil is:

Coarse sand	(2·0–0·2 mm.)	5·7%
Fine sand	(0·2–0·02 mm.)	45·4%
Silt	(0·02–0·002 mm.)	26·7%
Clay	(< 0·002 mm.)	19·5%

It could therefore be described as a silty loam. The soil contains about 2 per cent. organic carbon and has an exchange capacity of 10·1 m.e. per 100 g.

A sample of the soil was dispersed with 'calgon' (sodium polymetaphosphate) and an oriented flake obtained by sedimentation of material smaller than 2 microns on to a microscope slide. The X-ray diffraction pattern showed 7-, 10-, and 14-Å lines, the 7- and 10-Å lines being due to the presence of kaolin and illite respectively. As the 14-Å line disappeared on saturating the clay with NH_4, it was considered that this line indicated the presence of a vermiculitic clay. The relative proportions of these minerals were estimated as 40 per cent. illite, 40 per cent. kaolin, and 20 per cent. vermiculite.

The soil as sampled in the field was air-dried and passed through a $\frac{1}{2}$-mm. sieve before use.

Measurement of Soil Permeability

Soil permeability was measured by using a cylindrical brass permeameter (approx. 5 cm. diameter and 5 cm. high) connected to an adjustable outflow by rubber tubing. A constant pressure head was maintained above the soil packed in the permeameter, with an inverted 100-c.c. volumetric flask which had a graduated scale attached to the stem so that the pressure head could be readjusted when it was necessary to refill the flask.

Twenty grammes of soil were placed in the permeameter on top of a 3-mm. layer of sand (1–$\frac{1}{2}$ mm.) which had been previously wet with the appropriate solution. The permeameter was then tapped twenty times to pack the soil uniformly. This procedure gave a pad of soil 1 cm. thick. A Whatman No. 4 filter-paper was placed on the soil surface to avoid disturbance when liquid was being added to or taken from the permeameter. The soil was wetted slowly from below before flow was commenced. The sand had a permeability of the order of 1×10^{-1} cm. sec.$^{-1}$, the soil permeability was in the vicinity of 2×10^{-4} cm. sec.$^{-1}$ Examination after each permeability trial showed a sharp boundary between the soil and sand in the permeameter. The work was carried out at 21° C.

As the purpose of these experiments was to investigate the effect of electrolyte concentration on the permeability of the soil saturated with

various exchangeable cations, it was first necessary to bring the exchange complex into equilibrium with a concentrated solution of the appropriate salt and then to change to a series of percolating solutions of decreasing concentration, which would maintain the same cation status. To ensure the required condition of saturation the soil pad was leached for 12 hours with the strong solution; during this period about 400 c.c. of solution passed through the soil.

The decrease in permeability observed during this stage was attributed to the packing of the soil. This decrease amounted on an average to 20 per cent. in all cases except when molar NaCl was used, when the decrease was about 30 per cent. However, for the 3 hours immediately preceding the changing of the initial solution for more dilute ones, the decrease was less than $\frac{1}{2}$ per cent. per hour: at this stage the permeability for a number of samples varied between 2·0 and $2{\cdot}4 \times 10^{-4}$ cm. sec.$^{-1}$. During the course of this work it was found that if the decrease in permeability, obtained on adding a particular solution, was expressed as a percentage of the permeability after the initial decrease, difficulties encountered due to the variation in this value were eliminated. Therefore the results are expressed as a percentage decrease in permeability rather than as an absolute value.

So that the flow conditions in these experiments were not more drastic than those obtained in the field a macroscopic velocity of flow of 0·8 in. per hour was adopted.

1. *Permeability of Single Ion Systems*

The soil pad (1 cm. thick, 5 cm. diameter) was brought to equilibrium with the chloride of the required cation. When the solution was to be changed for a more dilute one, the excess was carefully removed with a pipette and the surface washed twice with 20 c.c. of the more dilute solution which was then to percolate through the soil. At this stage it was necessary to observe that the filter-paper sat loosely on the soil surface and did not restrict flow into the soil. A record of the permeability was obtained by measuring the volume of outflow at regular intervals.

(*a*) *Sodium-saturated soil*

The soil was saturated with the sodium ion by passing molar NaCl solution through the soil pad for 12 hours. The excess solution was pipetted off and the surface washed as previously described. A number of trials were carried out using a range of concentrations of NaCl. In Fig. 1 the percentage decrease in permeability, for the different NaCl solutions used, is plotted against time. The percentage decrease in permeability has been corrected for the differences in viscosity and density between molar NaCl and the solutions for which the permeability values are recorded.

When the solution $2{\cdot}5 \times 10^{-2}$ M NaCl had been flowing through the soil for 1 hour the percolate was observed to be turbid due to the presence of clay particles. The major decreases in permeability took place in the

first 2 hours after the solutions were changed and even when this decrease was large the permeability still decreased slowly with time after this period.

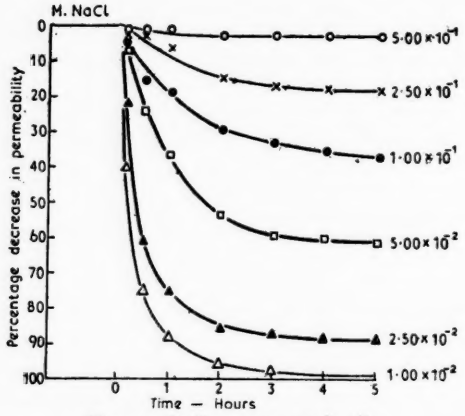

FIG. 1. Sodium-saturated soil.

The decrease in permeability for the sodium-saturated soil is thought to be due to swelling and deflocculation. Swelling would be expected to precede deflocculation, which was first observed at $2{\cdot}5 \times 10^{-2}$ M NaCl.

(*b*) *Potassium-saturated soil*

The soil was saturated with potassium by leaching with 0·2 M solution of KCl. The decreases in permeability obtained when this solution is replaced by more dilute solutions are shown in Fig. 2. The general

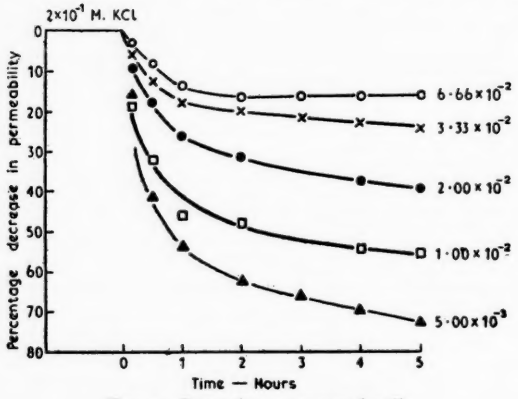

FIG. 2. Potassium-saturated soil.

appearance of these results is similar to those obtained for the sodium soil although the decreases occur at a lower concentration. For instance

the curve for 1×10^{-1} M NaCl is similar to the curve 2×10^{-2} M KCl. When the solution 2×10^{-2} M KCl was flowing through the soil pad slight cloudiness was observed in the percolate and when the concentration was 1×10^{-2} M there was definite evidence of clay deflocculation.

(*c*) *Magnesium-saturated soil*

The soil was saturated with magnesium by using a $3{\cdot}16 \times 10^{-2}$ M $MgCl_2$ solution. The percentage decrease in permeability when more dilute solutions are used are shown in Fig. 3. Decreases in permeability are obtained at a concentration below $3{\cdot}16 \times 10^{-3}$ M.

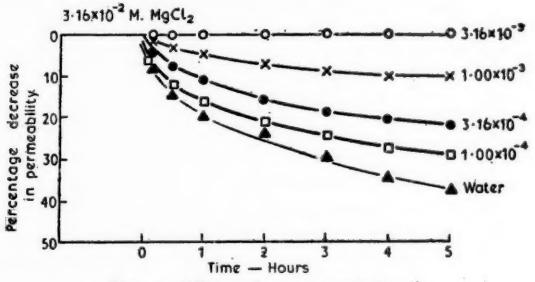

FIG. 3. Magnesium-saturated soil.

(*d*) *Calcium-saturated soil*

The soil was saturated with calcium by flowing 1×10^{-2} M $CaCl_2$ solution through for 12 hours. The decreases in permeability with more dilute solutions are small, and even when distilled water is used the decrease is about 25 per cent. in 5 hours. Small decreases in permeability were obtained when the calcium ion concentration was $3{\cdot}16 \times 10^{-4}$ M. Slight cloudiness was observed in the percolate when 1×10^{-4} M calcium chloride was used. The results for the calcium-saturated soil are shown in Fig. 4.

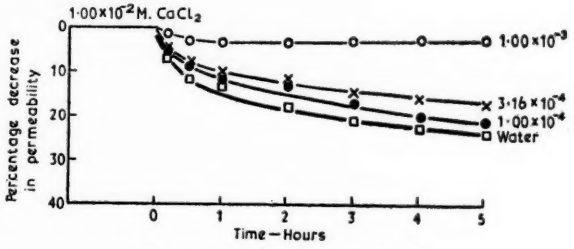

FIG. 4. Calcium-saturated soil.

Discussion

The concentration of salt which causes 10 to 15 per cent. decrease in soil permeability is defined as the *threshold concentration*. That is the concentration where factors which can cause drastic reduction in permeability are becoming operative. This concentration has no absolute

basis but is used as a convenient reference level. The threshold concentration for various soil modifications are given in Table 1 together with the pH of the soil measured in the same solution at the completion of the permeability test.

TABLE 1

Threshold Concentrations and pH values for Sawyers 1

Salt	*Threshold concentration molar*	pH
NaCl	$2{\cdot}5 \times 10^{-1}$	5·2
KCl	$6{\cdot}7 \times 10^{-2}$	5·4
$MgCl_2$	1×10^{-3}	5·4
$CaCl_2$	3×10^{-4}	5·4

In Figs. 1 and 4 it can be seen that the percentage decrease in permeability, obtained with solutions considerably less concentrated than the threshold concentration, was greatest for the sodium-saturated soil and least for the calcium-saturated soil. In fact for the calcium-saturated soil the permeability to distilled water is not very different from the permeability to 3×10^{-4} M calcium chloride; whereas the sodium-saturated material became almost impermeable when 1×10^{-2} M sodium chloride was used. The decrease in permeability to solutions more dilute than the threshold concentration was more marked the higher this concentration.

Results obtained by Quirk (1952) working with montmorillonite pads further illustrate the difference in behaviour of sodium- and calcium-saturated clays. For sodium-saturated montmorillonite a uniform rate of flow through the pads was obtained with 0·5 M NaCl solution. However, when this solution was replaced by 0·25 M the pads became visibly swollen and impermeable. Calcium montmorillonite retained its permeability to distilled water, changing only slightly below a concentration of 0·1 M $CaCl_2$. Norrish and Quirk (1954) have shown that this behaviour can be attributed to the crystalline swelling of montmorillonite. In a 0·5 M solution of NaCl an oriented flake of montmorillonite gave an X-ray spacing d(001) of 19 Å and at a concentration of 0·31 M the spacing was 40 Å. For calcium montmorillonite the spacing never increased beyond 19 Å.

Johnson and Norton (1941) have demonstrated a much lower viscosity (more dispersed) for sodium-saturated than for calcium-saturated kaolin in distilled water.

One point worth noting is that when aggregates of Sawyers 1 (75–150 microns) were subjected to sodium saturation and then a solution of 1×10^{-1} M NaCl was used the aggregates maintained their identity. Calcium-saturated aggregates of this soil were stable in distilled water. Following this work Emerson (1954) has shown that sodium-saturated aggregates fail at about $3{\cdot}4 \times 10^{-2}$ M NaCl but aggregates from grassland and soils which had received high dressings of farmyard manure were able to withstand much lower concentrations. Quirk, Samson, and Taylor (1952) found that if Sawyers 1 ($<\frac{1}{2}$ mm.) was treated with

krilium CRD189 (0·1 per cent.) it maintained a high permeability to 1×10^{-2} M NaCl, and hence, in this regard, krilium was behaving in the same way as soil organic matter.

The mechanism of the decrease in permeability is not entirely clear. However, three processes can be considered to be operative. These are:

1. *Swelling* results in the blocking or partial blocking of the larger conducting pores, and as flow through a pore is proportional to the fourth power of the radius, then appreciable decreases in permeability may result where the swelling is small.

2. *Failure* of the soil aggregates is brought about by stress resulting from unequal swelling throughout the soil mass. In this connexion organic matter is capable of acting to prevent failure.

3. *Deflocculation* can be regarded as occurring when the charged plates, which are moving apart in the process of swelling, have reached such a distance of separation that the attractive forces are no longer strong enough to oppose the repulsive forces. These forces between charged plates have been discussed by Verwey and Overbeek (1948) and Schofield (1946). In the permeability measurements with NaCl definite dispersion of the clay was obtained at a concentration of $2{\cdot}5 \times 10^{-2}$ M and this is close to the $3{\cdot}4 \times 10^{-2}$ M previously mentioned as the failure concentration for soil aggregates. It is conceivable that the mechanical action of failure is sufficient to cause particles to come into suspension.

2. *Flocculation Behaviour of Soil and Clay Suspensions*

Since deflocculation was observed during the permeability tests with the sodium-saturated soil, a study was made of the flocculation behaviour of a number of clays. Several clay minerals and soils, in which the type of mineral was known, were sodium saturated and a stable suspension of each was obtained. These include two montmorillonites, Wyoming bentonite and Red Hill (Surrey) montmorillonite, the latter being considerably finer and probably more representative of montmorillonites found in soils. Willalooka subsoil from Australia contains little organic matter and the clay mineral has been identified as illite. Rothamsted subsoil was chosen as it is rather similar to Sawyers 1 and would contain considerably less organic matter.

The quantity of NaCl required to bring about flocculation in 24 hours was measured and the results are given in Table 2.

From the table it can be seen that the other materials flocculate at much lower concentrations than Sawyers 1. Mattson (1929) has reported similar results. He found that a concentration of 1×10^{-1} M NaCl was required to flocculate a stable suspension of sodium-saturated Sharkey colloid which is montmorillonitic, whereas only 2×10^{-2} M NaCl was required to flocculate montmorillonite. It seems probable that organic matter is responsible for these observed differences in behaviour, and the work of Schofield and Samson (1953) gives support to this. In their study of the flocculation behaviour of kaolin it was found that the sodium-saturated kaolin was flocculated in distilled water (pH approximately 4). This material can be completely deflocculated by small additions of sodium hydroxide which increased the pH and resulted in the loss of

TABLE 2

Flocculation of Soil and Clay Suspensions

Na-saturated material	*Approx. particle size Å*	*Clay minerals*	*Molar concentration of sodium chloride*		
			Stable suspension	*Partially stable suspension*	*Flocculated suspension*
Sawyers 1 . . .	..	Illite* Kaolin Vermiculite	5×10^{-2}	1×10^{-1}	3×10^{-1}
Rothamsted sub-soil .	..	Illite† Kaolin	1×10^{-2}	..	2×10^{-2}
Willalooka sub-soil .	700	Illite‡	1×10^{-2}	2×10^{-2}	3×10^{-2}
Wyoming bentonite .	2,000	Montmorillonite	1×10^{-2}	..	$1{\cdot}4\times10^{-2}$
Red Hill montmorillonite	200	Montmorillonite	1×10^{-2}	$1{\cdot}4\times10^{-2}$	2×10^{-2}
Merck's kaolin . .	2,000	Kaolin	..	..	Distilled water

Clay minerals identified by *G. Brown, †D. M. C. MacEwan, ‡K. Norrish.

positive charges which they demonstrated were carried on the edge faces of this mineral at low pH values. They obtained further support for this idea when it was observed that only 0·15 m.e. sodium alginate per 100 g. clay were effective in producing stable suspensions without increasing the pH. In another experiment it was found that the kaolin clay treated with alginate (0·15 m.e./100 g.) required between 6×10^{-2} and 1×10^{-1} M NaCl to bring about flocculation. It was also shown that small quantities of montmorillonite or illite in the kaolin suspension were active in screening the action of the positive charges and hence gave stable suspensions.

The fact that alginate is effective in promoting the deflocculation of kaolin suspensions, together with the contrasting behaviour of Rothamsted sub-soil and Sawyers 1, suggests that similar compounds may be present in surface soils. 'On the basis of present information regarding the chemical nature of soil organic complexes the only compounds with effective carboxyl groups appear to be uronic acid complexes and oxidized lignins' (Bremner, 1951).

Sawyers 1 when calcium saturated was only partially flocculated at 1×10^{-3} M $CaCl_2$ and was completely flocculated at 2×10^{-3} M. For Ca-montmorillonite a stable suspension was obtained when the concentration was 3×10^{-4} M, and flocculation when this was increased to 5×10^{-4} M $CaCl_2$. Here again the effectiveness of some constituent of the surface soil in assisting deflocculation has been demonstrated.

The concentration where clay was first observed in the percolate from permeameters was $2{\cdot}5\times10^{-3}$ NaCl and this is about one-tenth of the concentration where complete flocculation takes place in suspension. In the previous section mention was made of the stabilizing effect of

organic matter. When, however, the material is in suspension organic compounds appear to act in a reverse manner and aid deflocculation.

3. *Permeability of Mixed Ion Systems*

In irrigation agriculture particular importance is attached to the presence of the sodium ion on the exchange complex; if the percentage of exchangeable sodium is greater than 15, the soil is classed as an alkali soil. Difficulties are encountered with alkali soils because, as a general rule, the irrigation waters used contain insufficient electrolyte to maintain the soil in a well-flocculated state.

The aim of this section of the work was to try and establish the quantity of electrolyte required to maintain a satisfactory permeability for soils saturated to varying degrees with sodium.

To carry this out the soil was brought to equilibrium with solutions having varying Na/Ca ratios. The soil in equilibrium with these solutions would then have varying degrees of sodium saturation. The end members, a sodium- and a calcium-saturated soil, have been discussed previously.

In this work it was necessary to bring the soil to equilibrium with a given Na-Ca solution and then to dilute so that this equilibrium is maintained. In this way the threshold concentration in equilibrium with the exchange complex can be found for each mixture. To do this it has been necessary to make one assumption, namely, that the percentage of sodium on the exchange complex is governed by the ratio of $(Na)/\sqrt{(Ca)}$ when appropriate corrections for the activities of the ions have been made using the principle of ionic strength. This assumption seems reasonable since each of the exchange equations of Gapon (see Kelley, 1948), Vanselow (see Kelley, 1948), and Krishnamoorthy and Overstreet (1949) can be arranged so that the exchangeable sodium percentage is a function of $(Na)/\sqrt{(Ca)}$ for the solution. Schofield and Quirk (unpublished) have examined this assumption theoretically. An analysis of the distribution of sodium between the diffuse double layer and the external solution has been attempted on the basis of the Gouy theory (1910). For a given value of $(Na)/\sqrt{(Ca)}$ this theory predicts a sharp increase of the amount of sodium in the diffuse double layer with dilution at high ionic strengths. This increase is followed by a stage during which the exchangeable sodium increases only slightly with further dilution.

Four series of Na-Ca solutions were used; the basic member of each series is as follows:

Series 1	1×10^{-2} M NaCl	1×10^{-2} M $CaCl_2$		
„ 2	2×10^{-2}	„	„	„
„ 3	5×10^{-2}	„	„	„
„ 4	1×10^{-1}	„	„	„

The soil was brought to equilibrium with one of these solutions and then a solution which was the most dilute solution of the series which would still maintain a constant permeability was allowed to flow through the soil for three hours before more dilute solutions were used.

TABLE 3

Exchangeable Sodium Percentages for Number of Na-Ca *Mixtures*

Series	*Molar concentration* NaCl	*Molar concentration* $CaCl_2$	% *exchangeable* Na
1	0·01	0·01	5·0
	0·00225	0·0004	5·8
2	0·02	0·01	8·1
	0·00448	0·0004	8·9
3	0·05	0·01	16·1
	0·01125	0·0004	21·0
4	0·10	0·01	32·2
	0·0227	0·0004	35 2

In Table 3 the exchangeable sodium percentage is reported for the basic member of each series and a member of each series which was slightly more concentrated than the threshold concentration. The latter solutions were used since more dilute solutions resulted in decreased permeability and made extraction difficult.

The exchangeable sodium percentages were determined by weighing the soil pad and entrained solution after equilibrium had been established and then extracting with a fifth normal solution of KNO_3. The cations in the extracted solution were estimated by the flame spectrograph.[1]

The results obtained by soil permeability measurements, by the method previously described, are shown in Figs. 5–8. From these

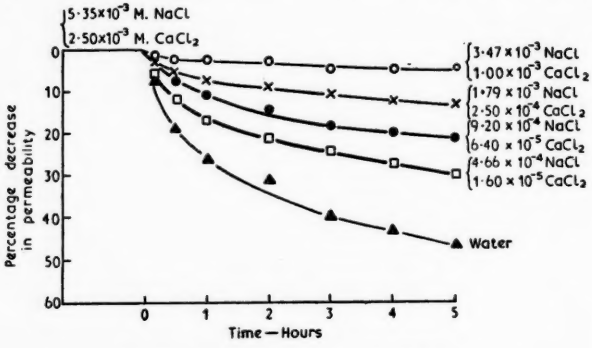

FIG. 5. Series 1—6 per cent. sodium.

curves it can be observed that when the Ca ion concentration is reduced to $2{\cdot}5 \times 10^{-4}$ M the decrease in permeability is in the vicinity of 10–15 per cent. The threshold concentrations for the various series are:

Series 1	$1{\cdot}79 \times 10^{-3}$ M NaCl		$2{\cdot}5 \times 10^{-4}$ M $CaCl_2$		
,, 2	$3{\cdot}58 \times 10^{-3}$	,,	2·5	,,	,,
,, 3	$9{\cdot}00 \times 10^{-3}$	,,	2·5	,,	,,
,, 4	$1{\cdot}8 \times 10^{-2}$	,,	2·5	,,	,,

[1] These determinations were made by Mr. H. A. Smith and Mr. H. H. Le Riche.

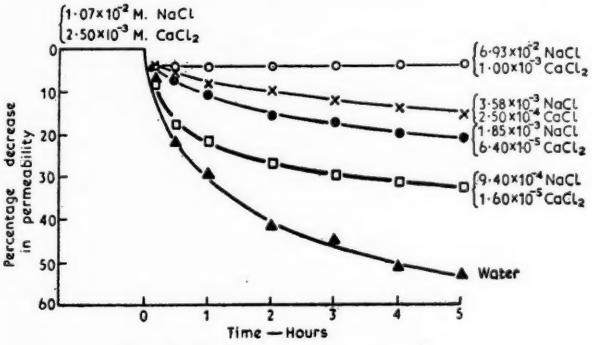

FIG. 6. Series 2—9 per cent. sodium.

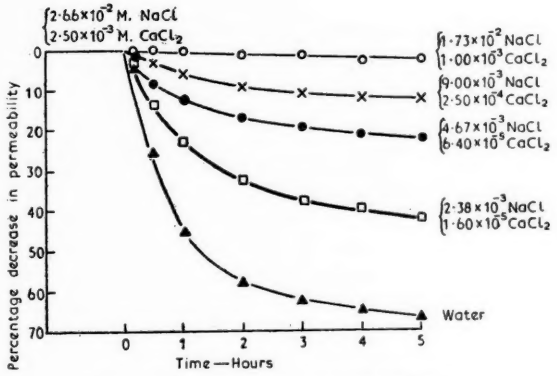

FIG. 7. Series 3—21 per cent. sodium.

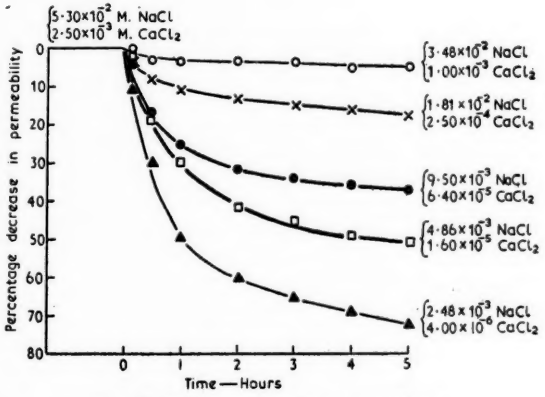

FIG. 8. Series 4—35 per cent. sodium.

Discussion

It is interesting to note that the threshold concentration for the mixed ion systems occurs when the concentration of divalent ion is reduced to the threshold concentration for the homoionic divalent system.

TABLE 4

Concentration of Electrolyte Required to Maintain Permeability for Varying Degrees of Sodium Saturation

Exchangeable sodium percentage	*Threshold concentration m.e./litre*	*Turbidity concentration m.e./litre*
0	0·6	0·2
5·8	2·3	0·5
8·9	4·1	1·0
21	9·5	2·4
35	18·6	4·9
100	250	25

In Table 4 the concentration of electrolyte required to maintain a satisfactory permeability of Sawyers 1 soil saturated to varying degrees with sodium is given. Greacen (1949) found that when the exchangeable sodium percentage of Yolo clay loam aggregates was 12, 5 m.e. per litre of electrolyte in the percolating water were not sufficient to prevent a decrease in the permeability. However, when this concentration was 20 m.e. per litre a satisfactory permeability was obtained. In the reclamation of sea-flooded soil in Holland, van Beekom *et al.* (1953) found that, 'The typical heavy decline in structure begins in the first winter after drainage when the soluble salts are largely removed from the top soil. Its first signs occur as soon as the concentration of common salt drops below 5 g. per litre.' This corresponds to 80 m.e. per litre and the exchangeable sodium percentage would be approximately 20. These workers state further that 'The crumb structure is only lost if the soil is stirred; therefore this only occurs in the layer that is ploughed and especially at the surface which is exposed to the devastating influence of falling raindrops.' This latter statement explains the divergence between the concentration of 80 m.e. per litre and that quoted in Table 4 for an exchangeable sodium percentage of 21. In the permeability test no mechanical action other than that of the flowing liquid was involved. In the previous section it was mentioned that turbidity in the case of the sodium-saturated clay was first observed at a concentration of 25 m.e. per litre yet a stable suspension of the clay required 300 m.e. per litre for complete flocculation. These results indicate that any mechanical action in addition to that of the flow through pores would result in a more rapid loss of permeability and structure.

The concentration of the solution which produced a turbid percolate from the permeameters is also given in Table 4. In general turbidity appears when the concentration of the percolating solution is one-quarter to one-fifth of the threshold concentration. It should be mentioned, however, that the degree of turbidity varied continuously

with the exchangeable sodium percentage. For the calcium-saturated soil turbidity of the percolate was only just discernible, whereas with the sodium-saturated soil very turbid percolates were obtained. The relationship between the threshold and turbidity concentration for the sodium-saturated soil appears somewhat anomalous, but this may possibly be explained by the fact that each is determined on concentration scales where a factor of two is involved in each dilution step.

From Fig. 9 the quantity of electrolyte required to maintain a stable

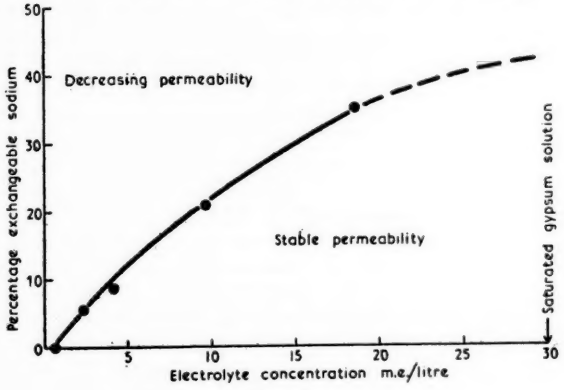

FIG. 9.

permeability, for any degree of sodium saturation, can be read off. It is necessary to consider to what extent this curve can be applied to soils other than Sawyers 1. From the work of van Beekom *et al.* (1953) and Emerson (1954) it is obvious that soils with high organic matter or soils just out of grass have more favourable properties when saturated to varying degrees with sodium than other arable soils in a similar condition. However, for soils of semi-arid and arid areas to which this work should mainly apply, the relationship is probably directly applicable with the possible exception that kaolinitic soils of low pH may not be as badly affected as soils containing other clay minerals.

To reclaim alkali soils Richards (1947) recommends the application of gypsum in quantities equivalent to the amount of exchangeable sodium in the soil. This procedure has the disadvantage that gypsum is not readily soluble and hence may not give a sufficiently concentrated percolating solution to prevent decreases in permeability when applied as a surface soil dressing.

The permeability studies show that there is no particular basis for the division of soils into alkali and non-alkali classes at 15 per cent. exchangeable sodium. As the exchangeable sodium percentages increase, the permeability to solutions considerably less concentrated than the threshold concentration decreases continuously.

Soils can be characterized by measurements made on the saturated extract. From the ratio $(Na)/\sqrt{(Ca+Mg)}$ the exchangeable sodium percentage can be calculated by use of the Gapon equation. The same ratio

together with the conductivity should also be obtained for the irrigation water. When these quantities have been found reference to Fig. 9 will show to what extent it may be necessary to modify the irrigation water.

4. *Application of the Threshold Concentration Concept*

The above results indicate that it should be possible to maintain the permeability of a soil irrespective of the degree of sodium saturation by using a sufficiently strong electrolyte solution or by the addition of gypsum or other soluble calcium salts to the irrigation water. For an alkali soil the aim is to replace the sodium by calcium. This is more efficiently done if the soil permeability can be maintained during the reclamation. However, if salts are used in the irrigation water to maintain a satisfactory permeability adequate drainage must exist for the removal of the salts. The solubility of gypsum at 20° C. is indicated on Fig. 9. In actual practice it is probable that only a half-saturated gypsum solution could be readily obtained and if a higher concentration than this were required then the more soluble calcium chloride could be used.

The usefulness of this concept is best illustrated by results obtained by McGeorge and Fuller (1950). Cajon sandy loam is usually irrigated with river water, but during the years 1946 to 1948 there was little river water available, and it was necessary to pump water from an underground supply. This water contained 50 m.e. of sodium and 8 m.e. of calcium per litre and the figures given for the exchangeable sodium percentage for a number of samples of the soil after irrigation with this water for 3 years vary between 19 and 34 with 25 as the mean. The value of 25 is in good agreement with a calculation using the Gapon equation for this water. Such a soil would require 11 m.e. of electrolyte per litre of irrigation water. These workers report that when river water was again available in 1949 the soil 'froze up'. (This would correspond to a 40 per cent. decrease in permeability in Fig. 7.) The river water contained only 3·9 m.e. of electrolyte per litre. If 8 m.e. of calcium ions were added to this river water for irrigation until the majority of the sodium had been replaced satisfactory soil conditions would have been maintained and it would then have been possible to use the river water without the addition of calcium for irrigation.

Alternatively if as little as one-sixth of the well water were added to the river water this trouble could have been avoided. This proportion could subsequently have been decreased until it was again possible to use river water alone.

Summary

Artificially packed pads (1 cm. thick, 5 cm. diameter) of soil $< \frac{1}{2}$ mm. from one of the Rothamsted fields were saturated with a given cation by leaching with a strong chloride solution of the ion for 12 hours. After this time a constant rate of flow was established. A series of successively more dilute solutions were then allowed to flow through the pads and the permeability was measured at regular time intervals for a period of 5 hours. Below a certain concentration which is specific for each ion decreases in permeability of the soil pads were observed.

The following threshold concentrations were obtained for the soil saturated with the appropriate cation:

$2{\cdot}5 \times 10^{-1}$ M NaCl
$6{\cdot}6 \times 10^{-2}$ M KCl
1×10^{-3} M $MgCl_2$
3×10^{-4} M $CaCl_2$

The flocculation behaviour of sodium-saturated clays suspended in distilled water has been examined. These materials (illite and montmorillonite) show a flocculation value of 2×10^{-2} M NaCl which is considerably lower than that obtained for the surface soil. It is considered that some constituent of the organic matter is responsible for this difference.

The threshold concentrations of electrolyte have been determined for the same soil having varying degrees of Na-saturation. Four series of Na-Ca solutions were used; the exchangeable sodium percentage for the soil in equilibrium with each of the series was 6, 9, 21, and 35. The threshold concentration for each series occurred when the calcium ion concentration in the mixed solution had been reduced to $2{\cdot}5 \times 10^{-4}$ Molar.

The concept of threshold concentration has not been previously applied to problems of irrigation agriculture. The usefulness of this concept is illustrated by data of McGeorge and Fuller for a soil from the Upper Gila River Valley, Arizona. It is therefore suggested that soils could be characterized by measurement of $(Na)/\sqrt{(Ca+Mg)}$ and the conductivity of the saturated extract, these values being determined for the irrigation water also.

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IMPROVEMENTS IN THE STRUCTURAL STATE OF SOILS UNDER LEYS

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Summary

An investigation was made of the time taken by a ley to change the physical state of an old arable soil to that of an old grassland soil so that, for example, its physical condition on ploughing is the same as that of old grassland on ploughing. The process was found to be slow, taking possibly 50 years or more on some clay soils. On coarse sandy soils the process may be considerably faster, e.g. 5–10 years.

Introduction

It has long been recognized that the physical condition of a soil, from the points of view of cultivation and crop growth, is at its best in the year or so following the ploughing out of an old pasture,[1] and that with arable farming this optimal condition is not maintained. In medieval Britain, to maintain soil fertility, two successive crops of cereals were usually followed by 1 year weed fallow which was grazed, the plants that grew during the fallow being self-sown. The deliberate sowing of grass and clover seeds for the resting period did not begin until the seventeenth century. During the eighteenth and nineteenth centuries the grass-clover break varied from 1 to 3 years, e.g. in the Norfolk four-course rotation it was 1 year, but in the north-west of England it tended to be 3 in a six-course rotation. Elliot (1898) suggested 'four to six years good turf on old arable land would restore it to a condition comparable with old pastures'.

During the twentieth century (apart from the war period 1914–18) ploughing of old grassland in Britain was rare until the outbreak of war in 1939 when it became commonplace. In many cases the contrast between the physical condition of this soil and that of corresponding old arable land was most marked. At Jealott's Hill, for example, the difference between the old and 'new' arable land in such matters as ease of cultivation, crop yields, &c., was striking. Such observations stimulated the question, how long does it take to restore old arable land to the physical condition of old grassland so that it has, for example, the same properties on ploughing and cultivating? It was realized that the answer might vary with soil type, seeds mixtures, climatic conditions, &c. Consequently it was decided to make observations on twenty-two farms in different parts of England and Wales on a variety of soils and with as much variation in climate as possible. On each farm it was aimed to have an old arable soil about to be sown to a ley and nearby an old pasture of the same soil type, preferably not ploughed within living memory, to act as a standard for comparison.

How was one to know when old arable land under grass was restored to the condition of old grassland? There appeared to be at least two

[1] Old pasture and old grassland have been used synonymously.

approaches to this problem. Either one could plough the ley[1] and compare its physical state and cropping capacity with old grassland ploughed at the same time (method A), or one could leave the fields unploughed and attempt to compare the physical state of the soils both *in situ* and on samples in the laboratory (method B). Although method A would have given a more definite answer, especially as the ultimate criterion of soil fertility is crop yield, it would have required complicated field trials which would have made it impossible to cover a wide range of soil types, &c. Consequently method B was chosen.

An experiment involving method A in which the influence of 1, 2, or 3 years of ley was contrasted with continuous arable farming has, however, been in progress at Jealott's Hill for some years and measurements of the type referred to below are being made.

A number of measurements and field observations can be made to decide when the optimal physical state is reached (Low, 1954). Measurements of crop yield and draw-bar pull on ploughing are clearly only suited to method A. For both methods A and B, one or more of the following can be used:

(i) infiltration and drainage rate, the former in the field, the latter on cores in the laboratory,
(ii) observations on the stability of soil aggregates to wetting and drying in the field (limited in the case of method B to such things as fresh mole hills, &c.), porosity, size and shape of aggregates, &c.,
(iii) measurements of the water stability of aggregates in the laboratory,
(iv) pore space at field capacity, &c.,
(v) 'available water' capacity.

In this paper a selection of the results obtained by using method B on the twenty-two farms already referred to are described, the criteria being limited to systematic field observations over a period of years and measurements of the stability of air-dry soil aggregates to wetting.

Methods used in the Field and Laboratory

Field examination of the structure of soil. The field studies have been generally descriptive. The main points considered have been (i) size and shape of the aggregates, (ii) size and shape of the pores and channels, and (iii) properties resulting from the types of aggregates and their distribution, such as compactness of the soil, stickiness, ease of breakdown of aggregates on crushing, &c. Observations on plant and animal life have also been made as they have been found to be of considerable help in studying the changing physical condition of the soil. Great importance has been attached to the activities of the soil fauna, particularly worms. A study has been made of the distribution of roots (including an estimate of the proportion of living to dead) together with indications of impeded drainage. A specimen of a field sheet used in the course of this work is given in the Appendix.

Field sampling. This has been described previously (Low, 1954).

[1] Defined by the Oxford Dictionary as 'arable land under grass'.

The sampling areas were 20 × 20 yd., and they were visited each spring and autumn, in some cases for 9 years. The area was as typical as possible of the field, and preferably near to its centre.

Water stability of air-dry soil aggregates. The process of preparing the sample from the field can be likened to the cultivation and preparation of a seed bed. The field samples were exposed in the laboratory until air-dry when they were gently crushed with a wooden pestle and mortar, and passed through a $\frac{1}{2}$-in. sieve to remove stones $> \frac{1}{2}$-in. The laboratory determination of aggregate stability has been described elsewhere (Low, 1954).

Water stability of air-dry aggregates: interpretation of the data

Examination of Fig. 1 shows that the percentage of water-stable

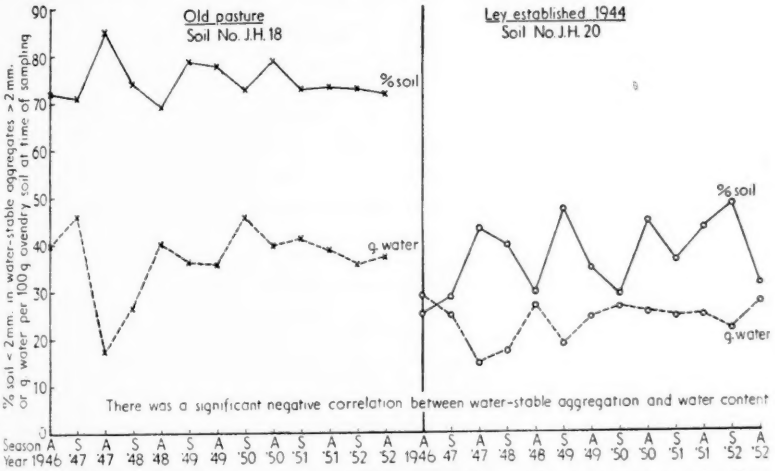


FIG. 1. **Relationship between water-stable aggregation and water content of soil at sampling (spring and autumn).**

aggregates > 2 mm. from a clay loam[1] in permanent pasture for at least 110 years (J.H. 18) has not been constant over the past $6\frac{1}{2}$ years. Comparison of the percentage of water-stable aggregates > 2 mm. with the water content of this soil at sampling time suggests that the lower the latter the greater the percentage of the former. A similar relationship is shown for a ley established in 1944 (J.H. 20), this field being of the same soil type and adjacent to J.H. 18.

That the variation in water stability was not due merely to field sampling errors is shown by the way in which the percentage of water-stable aggregates > 2 mm. has followed the same general pattern in four adjacent fields of the same soil type (J.H. 18–21 inclusive) all of which have been under grass for varying periods of time (Fig. 2). The trend for field J.H. 20 in 1944 and 1945 is different, but these were its first 2 years under grass.

[1] American textural nomenclature used throughout.

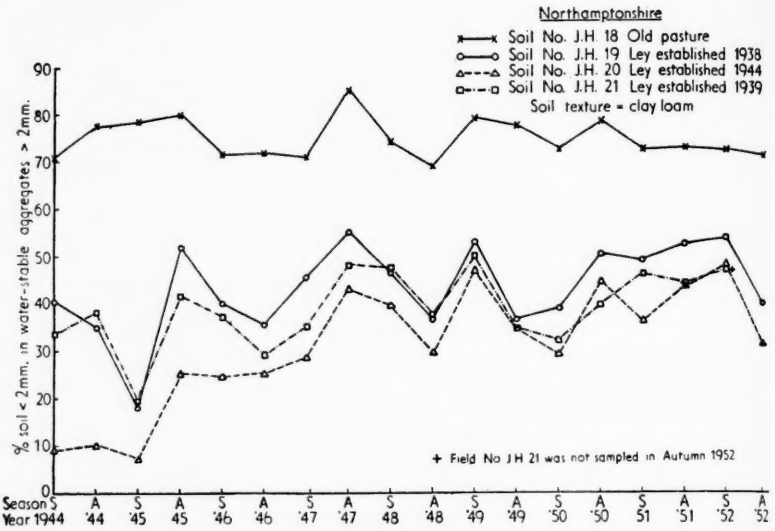

Northamptonshire
Soil No. J.H. 18 Old pasture
Soil No. J.H. 19 Ley established 1938
Soil No. J.H. 20 Ley established 1944
Soil No. J.H. 21 Ley established 1939
Soil texture = clay loam
% soil < 2mm. in water-stable aggregates > 2mm.
90
80
70
60
50
40
30
20
10
0
+ Field No J.H. 21 was not sampled in Autumn 1952
Season S A S A S A S A S A S A S A S A S A S A
Year 1944 '44 '45 45 '46 46 '47 47 '48 48 '49 49 '50 50 51 51 '52 '52 A

FIG. 2. Seasonal changes in water-stable aggregation in three leys and an old pasture.

Many fields have been sampled in different parts of England during the last 9 years and the same general relationship has been found between water content and percentage of water-stable aggregates > 2 mm. The drier the soil at the time of sampling the more water-stable the aggregates appear to be. This suggests that the drier the conditions in which ploughing and cultivations are carried out the more stable the structure (or tilth[1]) resulting from cultivations is likely to be. Farmers invariably claim that the best yields of cereals have followed ploughing under dry conditions in the autumn.

In addition to the variations in aggregate stability between spring and autumn, variations over 6-week periods (Fig. 3) and from day to day (Fig. 4) have been found. In each case the percentage of water-stable aggregates appeared to be related to the water content at the time of sampling. Variations of this type were first found in 1945 on two arable soils. The data for Figs. 3 and 4 were obtained in 1952 and 1953 in both cases on grassland. The recent work confirms the earlier.

Seasonal and other variations in aggregate stability have been observed by Hénin (1938 and 1939) and Hénin and Turc (1949), Kolodny and Neal (1941), Wilson and Browning (1945), Alderfer (1946), and Rowles (1948).

The dynamic nature of soil structure, from whatever angle it is studied, makes comparison over a period of time at a single site difficult. Owing to the possibility of considerable variations between any spring and the following autumn and from one year to the next, short-term studies

[1] Tilth is considered to be the structural state resulting from cultivation of the surface soil.

of the changes in aggregate stability of leys may be misleading. Apart from seasonal variations, aggregate stability of a ley does not always increase steadily with time (Fig. 2), but downward trends are usually

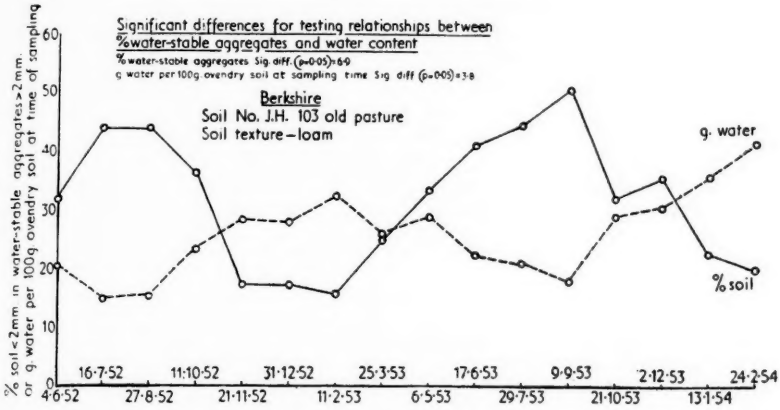
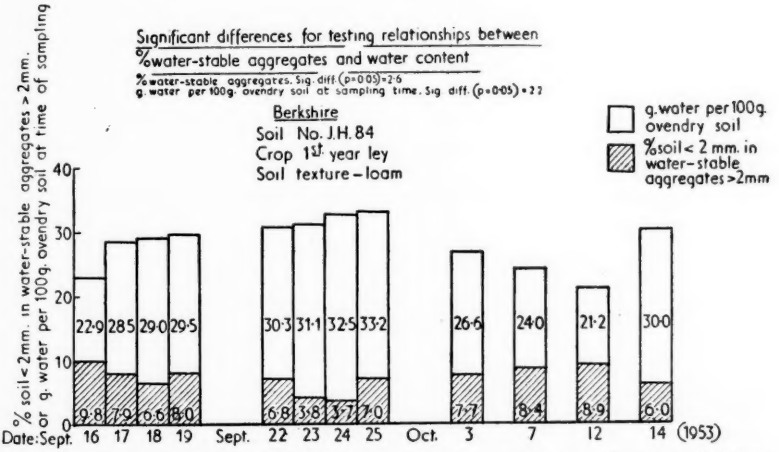


FIG. 3. Water-stable aggregation and water content of soil at sampling (six weekly intervals).



NOTE. These data suggest that relationship between water content at sampling time and water stability of the aggregates may not be simple. From the first two sets of histograms it is seen that with increasing water content there was first a fall in aggregate stability and then a rise.

FIG. 4. Water-stable aggregation and water content of soil at sampling (daily).

accompanied by corresponding changes in adjacent old pasture. As we have been attempting to find the time required for arable soils to reach the old-pasture condition, changes in aggregate stability of a ley

relative to corresponding old pasture have been measured (method (ii), p. 184).

At Jealott's Hill, two methods of setting out the results have been used, (i) plotting percentage of water-stable aggregates against time (Fig. 2), and (ii) calculating

$$\frac{\text{per cent. water-stable aggregates} > 2 \text{ mm. in a ley}}{\text{per cent. water-stable aggregates} > 2 \text{ mm. in old grassland}} \times 100,$$

which is referred to as the index of aggregation (hereafter as I.A.). Whilst the former shows long-term trends towards the condition of old pasture reasonably clearly, the I.A. is better over short periods. The I.A. will be 100 when the per cent. of water-stable aggregates of the ley is equal to the corresponding old-pasture soil.

Systematic observations and laboratory studies of the effects of leys on soils

No systematic study of the changes in the structural state of an arable soil after establishing a ley on it appears to have been made in Britain or elsewhere other than by Low (1950) who described the effects of leys of varying length on a clay loam soil in eastern England. He concluded that an old arable soil after 25 years of grass was not the equal, either in water stability or in structure as judged in the field, of an adjacent 110-year-old pasture on the same soil type. That paper dealt with the observations at one farm only, but as explained earlier, work has been conducted on twenty-two farms covering a wide range of soils. An account follows of the soils, field observations of structure, laboratory measurements of water stability of aggregates, management of the leys, &c., at a number of these farms. The mean I.A.s for each year have been given and summarized in histograms (Fig. 5). Where the initial observations were made in autumn, the mean for the autumn and subsequent spring is given. Some individual I.A.s are included in the text.

FARM NO. 1 *Cumberland.*

Parent material: glacial sand derived from Triassic sandstone overlying the Borrowdale volcanics.

Annual rainfall: 36·4" | *Soil*: texture—coarse sandy loam; drainage—free

Probable great soil group: podzol under heath or coniferous forest

*Year** of ley	*Management*	*I.A.*	*Mechanical analysis* %†			
				Coarse sand	*Fine sand*	*Silt*	*Clay*
1	grazed	..					
2	hay—good	77					
3	grazed	90					
4	grazed	88	Old pasture	53	20	14	13
			Ley	53	19	16	12

* Year of sowing (if in the spring) is first year of ley.

† In this paper, coarse sand = 2,000–200μ, fine sand = 200–50μ, silt = 50–2μ, clay = < 2μ. (All by Bouyoucos's hydrometer method.)

This field had been cultivated for many years before it was undersown in oats in 1943 with perennial ryegrass and white clover. The soil was first sampled in spring 1944 when a good ley had developed. Between spring 1944 and autumn 1946 when the field was ploughed, one hay crop (1944) was taken; at other times the field was grazed with either cattle or sheep, but never overgrazed. Root development was very good down to 6 in. at least. Worm and mole activity was marked.

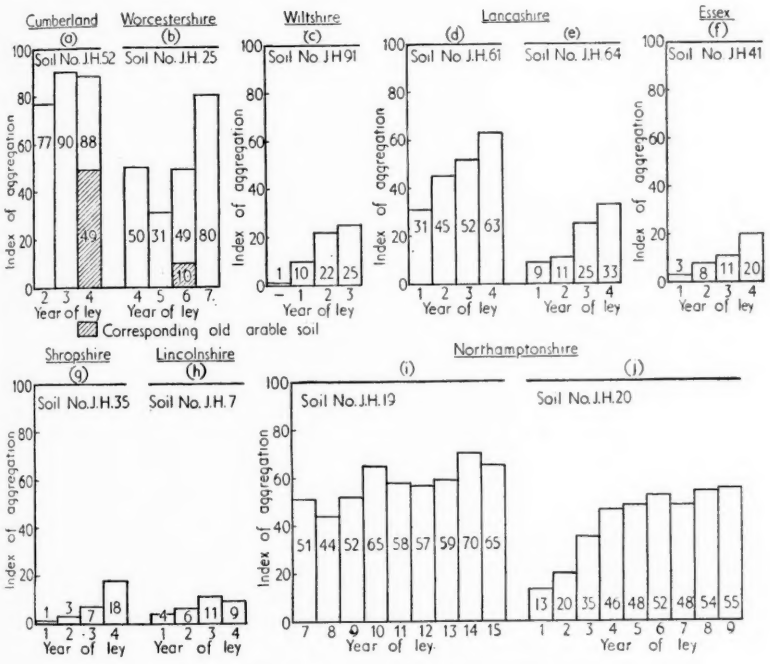


FIG. 5. Mean annual indices of aggregation.

From field observations little difference between the ley and the adjacent old-pasture soil could be detected in 1946 except that the latter was more mellow. The soil was not sampled before the ley was established, but an adjacent old-arable field of the same soil type and similar history was sampled in 1944, 1945, and 1946, and the I.A. was 49 in 1946 whilst that of the ley was 88. There seems little doubt that the initial I.A. of the ley was similar to that of the old-arable soil, the I.A. of which remained constant over the 4 years. It is important to note, however, that the overall extent of aggregation in both ley and old pasture was small, probably inevitably so, the soil containing much very coarse sand. The aggregates that were formed, although resistant to

slaking and sieving, were mechanically weak when dry. The water stability appeared to be largely due to binding by roots.

On a similar soil in Worcestershire, the I.A. did not reach 100 in 7 years. It was usually grazed harder (particularly year 5). When it was closed for hay (year 7 of ley) there was a considerable increase in I.A. (Figs. 5*a* and 5*b*).

FARM NO. 2. *Wiltshire*

Parent material: drift, mostly sand and flints overlying clay (Upper Greensand)

Annual rainfall: 29·4″ | *Soil*: texture—sandy loam; drainage—imperfect

Great soil group: meadow soil

*Year of ley**	*Management*	*I.A.*	*Mechanical analysis* %				
				Coarse sand	*Fine sand*	*Silt*	*Clay*
..	Arable	1					
1	Hay	10					
2	Grazed hard	22					
3	Grazed hard	25	Old pasture	36	29	21	14
			Ley	36	31	19	14

* First sampled in autumn.

This field had been arable for 10 years before being undersown in winter wheat in spring 1950 with ryegrass and white clover. There was a good 'take', the ley developing very well in 1951 when a hay crop was taken. After this the field was very closely grazed and this continued until the last sampling in May 1953. At the initial sampling in autumn 1949 when the field was arable no aggregates larger than coarse sand particles were observed. During the first year of the ley, root development was good and crumb-like aggregates about 4 mm. in diameter formed, but they were weak mechanically. After the hay crop, when the close grazing commenced, the soil became more compact and vigorous root development was not maintained. There appeared to be a slight rise in the worm population each year, the number being greater in autumn than spring.

In its third year the ley differed greatly from the old pasture both in structure and aggregate stability. It was much more compact, far less mellow to dig and appeared to be much less aggregated than the old pasture. During the first year of ley there was a marked increase in the I.A., from 1 in spring 1950 to 17 in spring 1951, when the field was closed for hay. This rate of increase was not maintained, being 22 and 23 respectively in the two following springs (see also Fig. 5*c*). This was possibly caused by overgrazing the sward. At the Worcestershire farm (Fig. 5*b*) the I.A. fell during heavy grazing and increased when a hay crop was taken.

The drainage was imperfect, rust coating some roots almost to the surface after a year of ley. This would have tended to prevent healthy root formation at least for part of the year and probably affected the development of stable aggregates.

FARM NO. 3. *Lancashire*

Parent material: Upper Boulder Clay overlying Keuper Marl

Annual rainfall: 35·2″ | *Soil*: texture—sandy loam to loam; drainage—imperfect

Great soil group: meadow soil

*Year of ley**	*Management*	*I.A.*	*Mechanical analysis* %				
				Coarse sand	*Fine sand*	*Silt*	*Clay*
1	Well grazed	31					
2	Well grazed	45					
3	Well grazed	52	Old pasture	22	32	31	15
4	Hay	63	Ley	20	27	31	22

* First sampled in autumn.

This field had been arable for many years before it was direct reseeded in spring 1944 with a ryegrass-clover mixture. It was first sampled in autumn 1944 when there was an excellent close-knit sward. The field was well managed by adequate manuring and grazing, avoiding poaching and winter grazing. Root development (0–6 in.) was markedly seasonal, being good in spring, but poor in late autumn when many were rust coated. Between 1944 and 1948 the worms increased, reaching between 500,000–1,000,000 per acre (0–6 in.). At the last sampling when the field was closed for hay there was a marked development of crumb-like aggregates, 3–4 mm. in diameter.

The initial I.A. (autumn) was comparatively high (29). It increased markedly in the 4 years following reseeding, the final value in spring 1948 being 64 (see also Fig. 5*d*). The structure as observed in the field improved very considerably and was becoming similar to the old pasture by spring 1948. The comparatively high I.A. reached, despite the imperfect drainage, was attributed to good management; at no time did the soil become really compact. The sward grew vigorously every year and was never grazed bare. It could be argued, however, that this I.A. was due to the relatively high initial value.

In Fig. 5*e* the I.A.s are given for another ley on soil of the same texture as that above. In this case the initial I.A. and the final after 4 years was lower than the field just described. It was grazed harder.

FARM NO. 4. *Essex*

Parent material: London Clay

Annual rainfall: 21·0″ | *Soil*: texture—silty clay; drainage—imperfect

Great soil group: meadow soil

Year of ley	*Management*	*I.A.*	*Mechanical analysis* %				
				Coarse sand	*Fine sand*	*Silt*	*Clay*
1	Undersown winter wheat	3					
2	Well grazed	8					
3	Well grazed	11	Old pasture	5	14	45	36
4	Well grazed	20	Ley	4	12	46	38

This field had been arable for many years before it was undersown in 1944 after being fallowed and mole drained at 22 in. There was quite a good take of seeds. A fair ley developed, largely of perennial ryegrass and white clover, which slowly improved in subsequent years, a good proportion of clover (30 per cent.) being maintained. The management was quite good; there was no grazing in 1945, 1946, and 1947 until well into the spring and at no time was any puddling seen. Although well grazed there was never any indication of overgrazing. In 1944 and 1945 the soil was sticky when wet, but this property had largely disappeared by the spring of 1946. Initially the aggregates were very angular and closely packed and it was not until 1947 (year 4 of the ley) that rounded crumb-like aggregates about 4–5 mm. in diameter were observed. These were limited to the 0–3 in. layer with angular aggregates, 10–18 mm. diameter, below. Root development was only fair in the earlier years, but by 1948 (year 5 of the ley) there was a moderate quantity in the 0–6 in. layer. In 1945 rust coating of the roots was observed, but this became less in subsequent years as the structure improved. There was an increase in worms, but even in the old pasture the number was small.

The I.A. was 4 in spring 1944 and 39 in spring 1948 (year 5 of the ley) a very considerable increase (see also Fig. 5*f*). From field observations there was a marked structural improvement, the proportion of visible pores increased and the soil became more mellow, but it was still very different from the adjacent old pasture. The air-dry aggregates here were much stronger than those at, for example, the Cumberland farm.

FARM NO. 5. *Shropshire*

Parent material: Upper Coal Measures—Keele Beds (red marls)

Annual rainfall: 28·0″ | *Soil*: texture—loam; drainage—fairly free

Probable great soil group: grey-brown podzolic

Year of ley	*Management*	*I.A.*	*Mechanical analysis* %			
				Coarse sand	*Fine sand*	*Silt*	*Clay*
1	Grazed hard	1					
2	Grazed hard	3					
3	Grazed hard	7					
4	Grazed hard	18	Old pasture	33	15	28	24
			Ley	30	17	30	23

This was an old arable field which, despite adequate manuring, was yielding very poor crops. It was direct reseeded with a ryegrass-clover mixture in the spring of 1944 which was also the time of the first sampling. There was an excellent 'take' of seeds and the ley looked well-established in the autumn. Despite adequate supplies of fertilizers and plenty of clover the sward did not grow well until 1947 (year 4 of the ley) when growth became quite vigorous. It was always grazed hard, usually by sheep. During the first year of the ley root development was quite good but it was small in subsequent years especially below 0–3 in. Development of crumb-like aggregates was slight and the soil remained very compact and 'closed' in structure, until the spring of

1947 when it became both much more porous and more mellow to dig. This coincided not only with a better sward but with a marked increase in worm population, which was estimated at 500,000 per acre (0–6 in.).

The initial I.A. of the soil (1 in spring 1944) was very low; by year 5 of the ley (spring 1948) when the field was closed for hay, it was 19 (see also Fig. 5*g*). Field observations indicated that the physical condition, after 4 years of ley, was much inferior to that of the corresponding old pasture. The final I.A. was much less than on Farm No. 4 due perhaps to the harder grazing or possibly the lower clay content.

On an old-arable soil in Lincolnshire a good sward was established, but after the first year was always very overgrazed; much more so than on Farm No. 5. The I.A. (Fig. 5*h*) showed little change over 4 years (4 to 9). There was less change on this farm towards the old-pasture state than on any other.

FARM NO. 6. *Northamptonshire*

Parent material: Chalky Boulder Clay (mostly from Oxford Clay which is the underlying rock)

Annual rainfall: 23·3″ | *Soil*: texture—clay loam; drainage—slightly imperfect

Great soil group: meadow soil—only slight gleying

Ley established 1944			*Ley established 1938*		
Year of ley	*Management*	*I.A.*	*Year of ley*	*Management*	*I.A.*
1	Barley undersown	13	7	Grazed hard	51
2	Grazed	20	8	Grazed	44
3	Hay	35	9	Grazed	52
4	Hay twice	46	10	Hay	65
5	Grazed	48	11	Grazed	58
6	Hay	52	12	Grazed	57
7	Grazed	48	13	Grazed	59
8	Grazed	54	14	Hay	70
9	Hay	55	15	Grazed	65

Mechanical analysis			
	Old pasture %*	*1944 ley* %	*1938 ley* %
Coarse sand	11	11	11
Fine sand	23	20	22
Silt	37	32	30
Clay	29	37	37

* Organic matter = 11%

Structural changes here were studied on three leys on very old arable land. In spring 1944 one field (J.H. 20) was in spring barley and undersown. The other two were leys established similarly in 1938 and 1939. The leys were adjacent to the pasture[1] standard which was at least 110 years old.

There was quite a good 'take' of seeds (perennial ryegrass and white clover) in the ley established in 1944. It was well grazed with beef cattle and never puddled. Hay crops were taken in 1946, 1947, 1949, and 1952. The ley was clovery (40–50 per cent.) until the latter part of 1951 when the proportion fell, becoming less than 5 per cent. in 1952.

[1] The soil on this old pasture, as a result of field drainage, probably represents the nearest approach to a chernozem in Britain (Low, 1951).

In the first 4 years root development was fairly good, but there was little increase afterwards. Incidentally the rate of increase in I.A. fell off after 4 years (see also Fig. 5*j*). In the first 2 years worms were few, but the number slowly increased and by 1952 was about 600,000 per acre (0–6 in.). During the 9 years of observations physical changes in the soil were clearly seen in the field. In the first 2 years the soil was

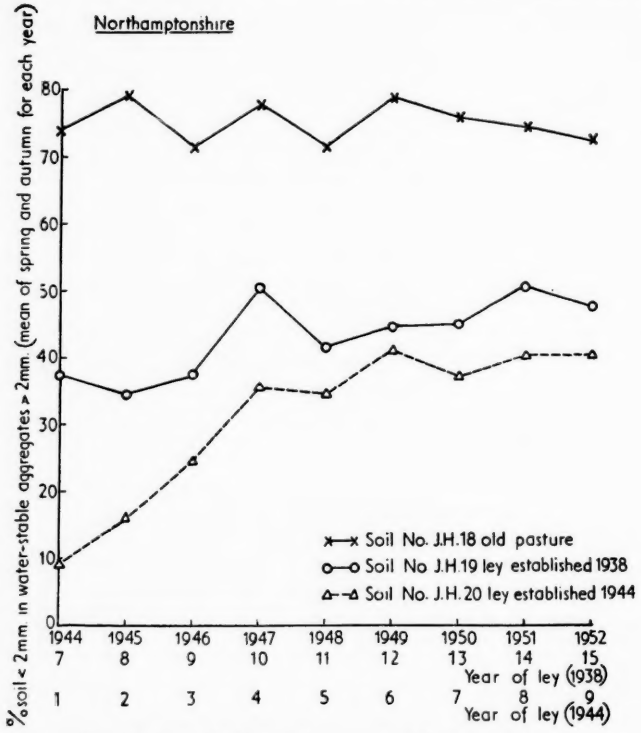


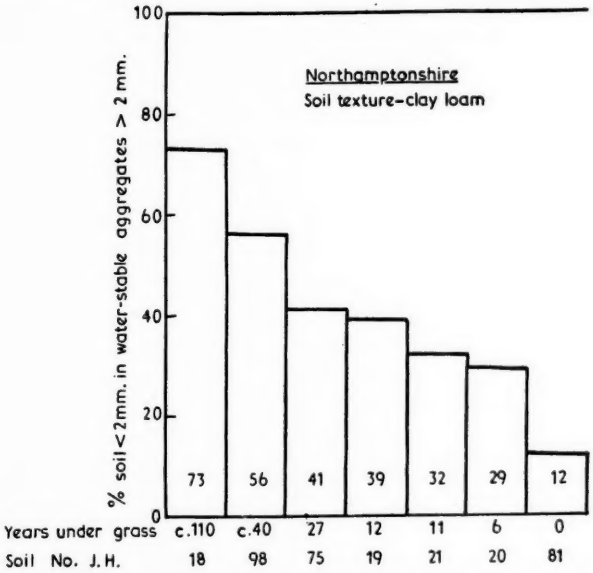
FIG. 6. Annual changes in water-stable aggregation.

very sticky when wet but it became much less so in 1946 and afterwards was hardly noticeable. This change seemed to be correlated with increased aggregation of the soil particles $< 50\mu$ (Low, 1954). Until spring 1946 the soil was very compact with few visible pores, but by then it was tending to break into hard angular aggregates, 2–3 cm. side. From then onwards the aggregates became smaller and less angular until by autumn 1952 they were about 5 mm. in diameter and somewhat rounded, but even then they were much more closely packed than those in the old pasture. It was difficult to distinguish in the field, even in 1947, any physical differences between the ley established in 1944 and those established in 1938 and 1939.

The I.A. at sowing was 12 and at the corresponding period in the

last year of sampling it was 66 (although the mean value for the year was only 55). Although there was a considerable improvement in its structural state, it was still much inferior to the old pasture (see also Fig. 6).

The ley established in 1938 (J.H. 19) was sampled first in spring 1944. It was a good ryegrass-clover ley grazed with sheep and beef cattle and was hayed three times in the first 6 years. It was steadily grazed for many months each year, but never poached. In 1944,



Field No. J. H. 75 was a poorer ley than any of the others but was the only one of its age available. Field No. J. H. 21 is discussed on this page. The S.E. of a single determinatiod was ±3·5 and of a mean ±1·8. A difference of 5·8 or more between two field means may be regarded as significant.

FIG. 7. Influence on water-stable aggregation of number of years under grass.

although the ley was in its seventh year, its structural state was much inferior to that of the old pasture. It was much paler in colour, the aggregates much more angular and closely packed, and there were less roots. Between 1944 and autumn 1952 the structural state slowly changed, the aggregates becoming rounder, smaller, more porous, and less closely packed, but was still much inferior to the old pasture. Root development increased, the quantity usually being considerably greater in the spring. Worms increased from about 500,000 to 2,000,000 per acre (0–6 in.). At the last spring sampling the I.A. of the 1944 ley was 66; the value for this ley was 75. (See also Fig. 5*i*.)

Similar comments apply to the 1939 ley[1] except that field observation usually indicated a poorer structure, i.e. more closely packed and more angular aggregates. It was usually more heavily grazed and often slightly poached. (It is noteworthy that with one exception structural differences

[1] Soil No. J.H. 21.

between the 1938 and 1939 leys observed in the field agreed with laboratory determinations of water stability of aggregates (Fig. 2). This was so to a remarkable extent on all the farms.)

In Fig. 6 the annual water-stable aggregation is plotted against time for the 1938 and 1944 leys. For the 1938 ley it shows only a slow increase from the seventh to the fifteenth year of the ley, whilst for the 1944 ley the rate of increase in water stability was rapid for the first 4 years, then declined, becoming similar to the 1938 ley.

The question, what is the time required to restore old-arable soil to the physical condition of old grassland has not yet been answered. At none of the twenty-two farms was the physical condition of old grassland reached, although on some of the very sandy soils it was approached, but the initial difference between old arable and old pasture on these soils was not great. In Northamptonshire, in addition to the four fields already considered, there were others which had been down to grass for different periods of time, and the water stability of the aggregates from them (all sampled on the same day) are shown in Fig. 7. An old arable field (J.H. 81) is included for comparison. It is clear that more than 40 years are required to restore this soil to the condition of 110-year-old pasture. Is there any evidence that 110 years has produced an upper limit in water-stable aggregation and the crumb structure characteristic of old grassland? The data in Table 1 suggests that an upper limit may have been reached at or before 110 years. No structural differences were observed between these two pastures in the field.

TABLE 1

Comparison of Water Stability of Aggregates from 110- and 400-year-old Pastures

Soil texture	*No. of years under grass*	*Soil no.*	*% soil <2 mm. in water-stable aggregates >2 mm.*
Clay loam .	*c.* 110	J.H. 18	71·7
Clay loam .	*c.* 400	J.H. 112	60·6

Standard error (single determination) ±4·5; significant difference 7·3.

Discussion

It is clear that under average farm conditions and with soils ranging from sandy loams to clays, many years are necessary to restore to an old arable soil the physical condition of old grassland.

It is useful to compare this conclusion with those reached in other countries. In the U.S.S.R. the general opinion has been that structure is restored by leys in 2 to 4 years (Lobanov, 1948; Williams, 1949; Vorobiev, 1950). Possibly the U.S.S.R. figures usually refer to very sandy soils; for only on sandy soils have we obtained an I.A. approaching 100 in 3 years (e.g. Fig. 5*a*). Further, Russians and Americans usually quote per cent. soil retained on a 0·25-mm. sieve; this tends to give a figure nearer that of the old pasture (Low, 1954).

Outside the U.S.S.R. there is neither evidence for such rapid restoration nor the same unanimity of opinion. Rounce (1949) in Tanganyika

could not detect any change in crumb structure of a light soil after 3 years of elephant grass. In the U.S.A. Olmstead (1946) found that after 7 years of grass the water stability of a soil was much smaller than that on virgin pasture on the same soil type with similar grasses. Jacks (1944 and 1949) from a survey of the literature concludes that soil structure can usually be restored in 2 to 5 years under grass.

An account of further observations concerned with structural improvement will now be given.

The influence of the composition of the sward on soil structure

The composition of the swards was similar at all the farms, being predominantly perennial ryegrasses and white clovers. At Jealott's Hill the effect of different mixtures on the structure of a sandy loam soil has been studied. There were three swards consisting of (i) pure grass (perennial ryegrass, cocksfoot, and rough-stalked meadow grass), (ii) clover dominant (70 to 90 per cent.), the remainder being self-sown meadow grass, (iii) a clover-grass sward with the grasses of (i) and the clovers of (ii), the latter forming 10 to 30 per cent. In one experiment the leys were maintained for 3 years, in another for 1 year. Under pure grass swards (1- and 3-year leys) rounded aggregates developed whereas with clover-dominant swards they tended to be larger and more angular. The grass-clover sward tended to give an intermediate condition. The difference in behaviour has been striking on ploughing both the 1- and 3-year leys. On the grass plots the furrow slice tended to collapse, giving a powdery tilth, whilst on the clover plots the aggregates tended to be large and angular, the furrow slice not breaking down readily. The water-stability results for the 3-year leys are given in Table 2.

TABLE 2

Effect of Composition of 3-year Leys on Water Stability of Aggregates

Date of sampling	*Description of plot*	*% soil <2 mm. in water-stable aggregates >2 mm.*
Sept. 1949 .	All plots just after sowing	1·3 (mean of 15 plots)
Sept. 1952 .	Grass	21·7 (mean of 5 plots)
	Grass-clover	24·2 ,,
	Clover dominant	22·3 ,,

The differences between the three swards were not significant.

The relative influence of legumes and grasses has been studied by Ward (1949) who found grasses superior to legumes on sandy and the converse on clay soils. Martin (1944) in Uganda and Tsyganov (1948) in the U.S.S.R. found grasses better than legumes, the former finding the difference small. Ackerman and Myers (1943) found lucerne better than grasses, but the legume received more manure. Page and Willard (1946) and Baiko and Suchalkina (1950) found the effect of grasses on structure was enhanced by addition of legumes, the former using lucerne. In these comparisons there is no indication that the grasses

received nitrogenous fertilizers as at Jealott's Hill. Here the comparison was between clovers (white and red) and grasses, whereas the literature usually refers to legumes, with lucerne occasionally specified.

Soil structure and worm activity

Structure improvement under grass often appeared to be linked with worm activity. A rough estimate of the number of worms per acre (0–6 in.) was made by counting the number in each of the ten holes ($6 \times 6 \times 6$ in.) at each sampling. Although these figures are only approximate they give indications of the trend over a period of years. The holes were dug very quickly and worms of all sizes were found and counted. In many cases the number, when the ley was established on old-arable land, was about 30,000–40,000 with 2,500,000–3,000,000 on adjacent old grassland. As the ley became older the worm population tended to increase, but there were no indications of a steady rise. This was hardly to be expected because of seasonal variations in soil conditions, &c. It is presumed that increase was related to increasing food supply. Their activities increased the proportion of larger pores which appeared to coincide with better root development.

The effect of soil structure and worms on root development

The effect of the structure of the soil on root development of grasses and clovers at the time of ley establishment has been observed on several farms. For example, some old-arable soils developed over Weald Clay, very poorly aggregated and water-unstable, were sown to Kentish ryegrass and Kentish white clover in 1944. Fair swards developed which were close-grazed by sheep. The soils soon become very compact and root development and ley productivity were limited, although there was a small increase in water stability. One field was ploughed in 1949, another in 1951, both in late winter. The latter was direct reseeded, the former after a pea crop, using the same seed mixture as in 1944. In both a very good tilth was obtained in the seed bed, and exceedingly vigorous and productive leys developed, in marked contrast to 1944. During the first leys worm activity, which was initially slight, slowly increased; after ploughing it increased greatly. When the second leys were sown, although the soil aggregates were much less water-stable than those of the old pasture a very porous structure was maintained by *worm activity*. After 1 year, despite fairly hard grazing by sheep, root development in the 0–6 in. layer was excellent and superior to that in the adjacent 50-years-old pasture. Nevertheless the indications were that the continuous close grazing would prevent this root development being maintained.

Changes in water stability of soil aggregates with distance from soil surface

Comparisons have been made between samples from 0–6 in., with 0–3 in., and 3–6 in., both taken from the same slice, also 6–12 in. and 12–18 in. in some instances; see Table 3.

The root development in Kent was poor below 0–3 in., in agreement

with the difference in aggregate stability. Similarly, in Derbyshire root development was much poorer between 6–12 in. as compared with 0–6 in. In the Northamptonshire old pasture there was good root development to at least 12 in. The lower value for 0–3 in. compared with 0–6 in. is noteworthy, possibly due to a shortage of active roots. The lower value already referred to for the water-stable aggregation of the 400- compared with 110-years-old pasture on this farm may be a development down the profile of this phenomenon. In the Northamptonshire ley, aggregate stability in the 3–6 in. layer was not much less than that in the 0–3 in., but there was not the marked difference in root development between these two layers as in Kent. It is remarkable that the aggregate stability at 12–18 in. in the old pasture (J.H. 18) should be considerably greater than in the 0–6 in. layer in the ley (J.H. 20).

TABLE 3

Variation in Aggregate Stability with Distance from Soil Surface

County	*Soil texture*	*Type of sward and site number*	*Date*	*% of soil <2 mm. in water-stable aggregates >2 mm.*				
				Depth of sample in inches				
				0–3″	3–6″	0–6″	6–12″	12–18″
Kent .	Loam	Ley 1943 J.H.3	Spring 1950	4·97	0·88	2·66	..	..
Derbyshire	Loam-silt loam	Old pasture 70 years J.H. 26	Autumn 1949	..	..	69·35	22·01	..
Northamptonshire	Clay loam	Old pasture 110 years J.H. 18	Spring 1950	64·10	74·84	72·59	63·27	50·79
	Clay loam	Ley 1944 J.H. 20	Spring 1950	28·09	23·26	28·84	26·23	..

Soil drainage and aggregate stability

It has been suggested earlier in this paper that poor drainage may adversely affect structural improvement. In an old pasture in Northamptonshire with ridge-and-furrow drainage, differences in water stability of the soil aggregates from the top of the ridge and bottom of the furrow (both 0–6 in.) have been found—Table 4.

TABLE 4

Influence of Degree of Soil Drainage on Water Stability of Aggregates

Sampling position	*% soil <2 mm. in water-stable aggregates >2 mm.*
Ridge (well drained) . . .	77
Furrow (poorly drained) . . .	59

The difference between ridge and furrow results was highly significant. The S.E. for a single determination was ±1·8.

There were no signs of impeded drainage in the soil on top of the ridge, but in the furrow the roots were rust-coated almost to the surface. Similar differences in aggregate stability have been found between old pastures of similar soil texture but with different drainage. The differences may be due to root development, as poor drainage causes its restriction and where there is seasonal flooding the roots are often killed.

The effects of roots on soil structure

Field observations of poor structure[1] in sandy soils showed that little aggregation with fairly close packing was their chief characteristic, whereas with clay soils it was aggregation into a coherent mass with little visible evidence of effective pores.

In the sandy soils, provided the fine sand content was not high, the roots were able to push their way between the sand grains and bind them into aggregates. Although such aggregates were often reasonably water-stable, they were mechanically weak. Formation of such aggregates on a considerable scale took place quickly, i.e. in a few months.

In wet clay soils with only a micropore space, root movement was impeded. In such soils it took place more rapidly as they dried, roots developing in the cracks that formed. The structural improvement depended to a considerable extent in the first instance on the weather, soil drainage, type of clay minerals, &c. Structural improvement in these soils was slower than in the coarse sandy loams, &c.

In our work the most difficult soils from the point of view of structural improvement have been those low in coarse sand or clay but high in fine sand and/or silt. Where the aggregates in such soils had broken down, a very closed structure had developed through which roots of a young ley could not move freely when the soil was moist and when they dried out there was little formation of aggregates as there was little shrinkage.

That soil aggregates slowly became more water-stable under a ley has been assumed to be due to protection of the clay colloids by organic colloids resulting from the breakdown of organic matter.

Discussion and Conclusions

The aim of this investigation was to find the time required to restore to old-arable land the physical state of old grassland using as criteria field and laboratory observations. It is concluded that in England this restoration usually takes more than 2 to 4 years, thus differing from findings in the U.S.S.R. The physical state of old grassland was not reached at any of the twenty-two farms and, on some, 3 to 4 years of ley produced only small changes. Nevertheless it is hoped to show in a later paper that even these small changes may be of significance in terms of crop yield.

[1] In a soil of poor structure the arrangement of aggregates results in low total porosity, e.g. 40 per cent., and a small proportion occupied by air at field capacity, e.g. 5 per cent. (both of the soil volume). A soil has a good structure if the total porosity is, e.g., 60 per cent. and the proportion occupied by air at field capacity is 20 per cent. (both of the soil volume).

The rate of physical improvement of old-arable soils sown to leys has been shown to depend upon a number of factors which include:

(i) The initial physical state of the soil: e.g. the higher the water stability of the aggregates the more quickly can a better physical state be built up.

(ii) The management. This seems very important. If fields are so grazed that the soil is closely compacted and root development restricted, structural improvement is greatly hindered; movement of the soil fauna, e.g. worms, is made more difficult. It was observed frequently that water-stable aggregation was greater in samples taken after hay crops, also after periods of vigorous growth. Liberal manuring with F.Y.M. and inorganic fertilizers seems necessary to give vigorous growth. The results of this investigation suggest that where a soil condition resembling old grassland is required, it is probably best to plough the ley and reseed after about 4 years.

(iii) The drainage. In poorly drained soils, either permanently or seasonally wet, plants tend to have either poorly developed root systems or most of their roots killed off from time to time. In so far as the roots of grasses and clovers are a major factor in the physical restoration of old arable land, any process which tends to limit their development will retard this process.

(iv) Mechanical composition of the soil. Structural changes appear to take place more rapidly in soil of either high coarse sand or clay content. In soils of medium clay and high fine sand and/or silt content, the processes tend to be much slower. Reasons have been suggested earlier in this paper (p. 196).

Whilst it has been found that in general 3–4 years are insufficient to restore to old arable land the physical state of old grassland, nevertheless some positive information has been obtained about the time required. On clay loams 50 years or more may be necessary; on sandy loams, with free drainage, it may be completed in 5–10 years.

The Director of Jealott's Hill, Dr. A. H. Lewis, initiated this work, and with the assistance of Mr. A. G. Strickland, selected the original sites in 1944. The author of this paper has been responsible for the work from 1945 onwards. He is greatly indebted to Miss F. J. Piper for her invaluable work both in the field and the laboratory.

APPENDIX

Specimen Field Sheet

Soil Structure — *Field Observations*

Farm..... Field Name ..... Date .....

..... O.S. No..... Weather.....

..... J.H. No..... .....

1	Feeling to spade		Compact	Mellow
2	Moisture (Kreybig scale)		o Air dry + Just moist ++ Moist-colour change	+++ Wet, no colour change ++++ Waterlogged
3	Colour			
4	Stickiness	To spade:	To boots:	
5	Handling	Plastic	Crumbles	
6	Tossing into air	Size and shape of aggregates:	If grassland, extent held together by root	
7	Appearance of aggregates including changes with increase in depth	Depth	*Grassland aggregates* Size. Shape. Soft. Hard.	*Arable land aggregates* Size. Shape. Soft. Hard.
8	Porosity	Closed Fissured	*Porous* Proportion pore size 1 mm. = ,, 1– 3 mm. = ,, 3– 5 mm. = (worm holes) 5–10 mm. =	
9	Worms	No. per hole (6″×6″×6″)	Worm casts..... Internal External	
10	Mole-hills	Old New	*Aggregates* Size: Shape:	
11	Rabbits			
12	*Vegetation* *Grassland* Grasses Clovers Root development *State of development*		*Arable* Crop Root development Weeds	
13	Erosion			
14	Comparison of structure with either permanent grass standard of same type or old arable soil			
15	Yield of crop			
16	Management: *Grassland* Hayed Grazed		*Manuring* F.Y.M. Fertilizers	Cultivations Root residues
17	Notes			

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WATER SORPTION AND SWELLING OF CLAY BLOCKS

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THE shrinking and swelling of clay soils early occupied the attention of Haines (1923), who recognized its widespread practical implications. He made the valuable start of defining two stages in the shrinking process, one of which he termed residual shrinkage as that stage where volume change of the soil is less than the volume of water withdrawn. The other stage, termed normal shrinkage by Keen (1931) in his discussion of Haines's experiments, refers to a volume change of the soil equal to the water content change. Normal shrinkage continues while the pore space remains saturated and is succeeded by residual shrinkage as unsaturation develops until, eventually, shrinkage ceases.

The relation of the two stages of the volume change process to the soil moisture tensions corresponding to them has not been reported, except incidentally. Hardy (1923), who measured the shrinkage of moulded clay blocks, mentioned that his 'soils ceased finally to shrink when the moisture content of the plastic brick had been reduced to a point which approaches the hygroscopic coefficient'. According to his data this would correspond to pF 5·0. The data of Lauritzen and Stewart (1941) on Houston black clay blocks showed that the volume change was normal at water contents near the wilting coefficient. Schofield (1938), discussing the data of Haines, considered that the transition from normal to residual shrinking occurred at about pF 5·0.

Further evidence of the quite high soil moisture tensions at which volume change of clay can continue has been given by recent field measurements (Aitchison and Holmes, 1953) of the seasonal vertical movement of two clay soils near Adelaide, South Australia. These soils, which were described as a red-brown earth (Soil type RB3) and a black earth (Soil type BE1) had caused damage to brick and masonry houses built thereon, if foundations were not designed to cope with the seasonal movements.[1] The volume change of these soils as related to the associated water content change was measured within the limits imposed by field experimentation. The present work began with the intention of describing, by more precise laboratory techniques, the swelling behaviour of the clay and it has led as well to a study of hysteresis effects in swelling and water sorption.

Experimental Methods

Material from these Adelaide soils was used in the investigation to be described. Red clay from the B horizon of the type RB3 soil and black clay from the surface horizon of the type BE1 soil were chosen because these two materials had exhibited the greatest amount of volume change

[1] Haines quotes the dry summer of 1921 as causing similar trouble to houses founded on the clay soils of southern England.

in the field. Their particle size analyses and densities are shown in Table 1. The clay minerals are predominantly illite and kaolinite, with small amounts of montmorillonite.

TABLE 1

Particle Size Analysis and Density of the Red and Black Clay

	Red clay	*Black clay*
Coarse sand: 2–0·2 mm.	1%	3%
Fine sand: 0·2–0·02 mm.	20%	22%
Silt: 0·02–0·002 mm.	15%	10%
Clay: <0·002 mm.	64%	65%
Density of solids (g./c.c.)	2·72	2·64

The material was broken by hand to about 2 cm., air-dried, and mixed in a concrete mixer. The portion needed was crushed and sieved through a 2-mm. round aperture sieve, the small amount of the material not passing at the second crushing being discarded. It was again mixed in the concrete mixer. Finally, it was dried for 24 hours at 50° C. before bringing to the required initial water content.

Moulded blocks, measuring 2·3 cm. diameter × 3 cm. high, were made from this material and these were the units upon which volume and moisture tension measurements were made. The water content at making of the blocks was 0·23 g./g., this being about the optimum for maximum compaction, with the procedure used. It was obtained by mixing the dried clay with the required amount of water. Spraying with an atomizer was unnecessary because the water was distributed uniformly enough by the pressure of moulding. Each block was made in a cylindrical mould the ends of which were closed by movable pistons. A 1-ton hydraulic jack applied a moulding pressure of 160 kg./cm.^{2}, which was measured by suitable inclusion of a proving ring in the assembly.

Measurements were made within the soil moisture tension limits of pF 6·0 and 2·0. The part of this range from pF 6·0 to 5·0 was obtained by allowing the blocks to reach equilibrium with water vapour over a saturated salt solution in a vacuum desiccator. The pressure membrane apparatus was used in the pF interval 4·0 to 3·0. For wetting the blocks, this apparatus was modified in the way suggested by Tanner and Hanks (1952). The suction plate technique provided tensions below pF 3·0. Richards's (1949) method of mounting a porous ceramic plate in a neoprene sheet was followed. The degree of vacuum was controlled by bubbling through a number of water columns in series. A similar apparatus has been described by Wilcox (1950) for regulating pressures greater than atmospheric to be applied to the pressure membrane apparatus. But a number of modifications have to be made if a controlled degree of vacuum is required. A diagram of the apparatus is shown in Fig. 1.

The pressure reduction to the vacuum manifold, *A*, was given by a glass capillary leak, *B*, included in the line. This leak was by-passed by a tap which could be opened, on setting up, to pump out the apparatus

quickly. The suction applied to the suction plate, C, was given by $(H_1+H_2+\ldots-h)$ cm. of water, where H_1 &c. are the heights of the water columns and h is the head of the reservoir for the plate. This neglects pressure effects of the bubbling which are small.

The pump was a converted compressor capable of reducing the pressure to about 7 cm. Hg. It was called on automatically when required by contacts in a mercury manometer and a relay circuit.

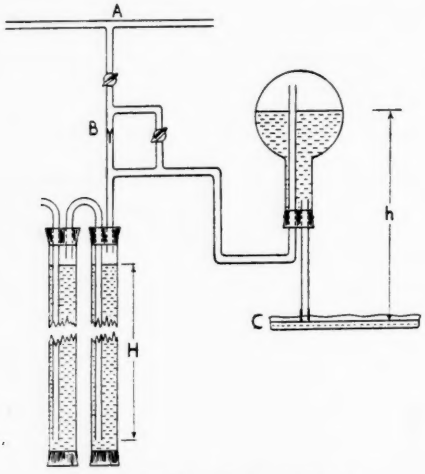

FIG. 1. Suction plate apparatus.

When the water content of a clay block had reached an equilibrium value at the required soil moisture tension, the volume of the block was measured. The apparatus for this was similar to one used in the Building Research Station, England, which employs the displacement of mercury principle. A volume of 10 c.c. can be measured to about 0·5 per cent. The block volumes were measured at a temperature of 20° C. ±1°.

The measurement of the water content and volume of the blocks at a given soil moisture tension provided the data from which Figs. 2 and 3 were constructed. Each experimental point is the mean of measurements on two blocks, with the exception of the starting-points of the pF curves. These represent the means of all of the blocks which were subsequently used, in pairs, to obtain the individual points defining the curves.

Swelling and Water Content

The swelling behaviour of the blocks is conveniently described by reference to their degree of saturation. This is the fraction, S, of the total pore space occupied by water and is given by

$$S = G_s \frac{w}{e}$$

where w is the water content, e is the voids ratio, and G_s is the specific gravity of the soil solids. If the degree of saturation does not change for a change in water content, this means that the pore space has enlarged or contracted by a volume equal to the water content change. Such is seen to be substantially the case for the red clay blocks, shown in Fig. 2, at water contents above about 0·17 g./g., and for the black clay blocks,

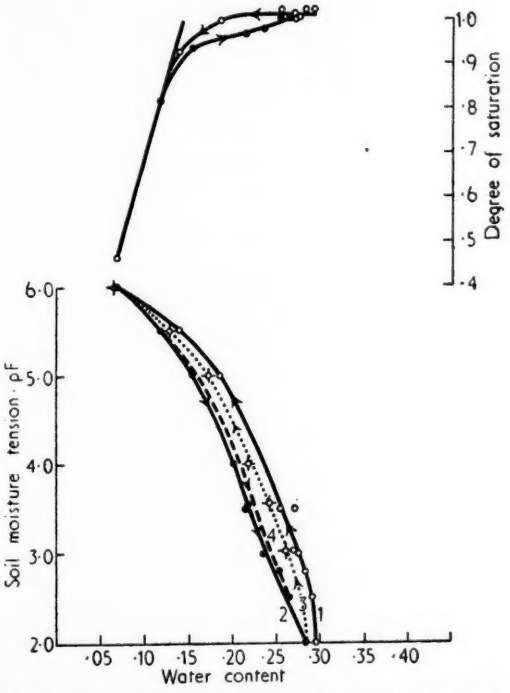

FIG. 2. Soil-moisture tension and degree of saturation of red clay blocks.

shown in Fig. 3, at water contents above about 0·16 g./g. This region of normal volume change, where the degree of saturation remains approximately 1·0, has a somewhat gradual transition to residual volume change at water contents below those quoted, when the degree of saturation diminishes for diminishing water content.

The degree of saturation has two values for a given water content in part of the range of measurement, according to whether the blocks make a wetting or a drying approach to equilibrium. This hysteresis, which is small, is no doubt the result of air having been trapped in the pore space on rewetting. It should be emphasized that all the experimental points represent blocks which have come to that position directly from the start of the curves in question. This would be favourable to the development of this kind of hysteresis.

The straight line, which has been drawn in both Figs. 2 and 3, represents the degree of saturation for changing water content if the voids ratio could be kept constant (i.e. no swelling) and equal to the smallest measured when the blocks were driest. The intersection of the straight line with the horizontal axis at degree of saturation equal to 1·0 divides the total water sorption into the ratio of the amounts contributed by

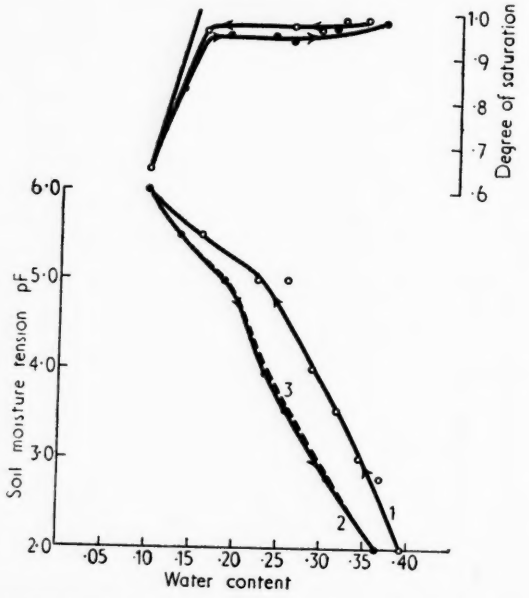

FIG. 3. Soil-moisture tension and degree of saturation of black clay blocks.

pore-space filling and pore-space enlargement. It can be seen from Fig. 2 that volume change ceased when the water content of the red clay blocks was reduced below 0·12 g./g. In the case of the black clay blocks (Fig. 3) volume change did not entirely cease at the limit of measurement.

Swelling and Soil Moisture Tension

The soil moisture tension–water content relationships for the red clay and the black clay blocks are also given in Figs. 2 and 3. From these and the degree of saturation curves it is possible to read off the moisture tension at which the transition from normal to residual shrinkage occurs and that tension at which volume change ceases. These are set out in Table 2.

The use of the moisture tension–water content relation for pore-size calculations is obviously restricted in the case of a swelling material when the pore size is changing. Table 2 gives the pF of the clay blocks at which their pores first begin to empty, on drying. An application of

TABLE 2

Soil Moisture Tensions Corresponding to Volume Change Stages

	pF of transition from normal to residual shrinkage	*pF at which volume change ceases*
Red clay blocks .	5·1	5·7
Black clay blocks .	5·5	>6·0

the Kelvin Equation, therefore, furnishes the size of the largest pores contained by the blocks when at this transition stage. These are, for the red clay blocks, a pore diameter of 0·023μ and, for the black clay blocks, a pore diameter of 0·009μ. But no general significance attaches to the transition point from normal to residual volume change since it is clearly governed by the particle size distribution of the material (see Stirk, 1954).

Hysteresis in the Moisture Tension–Water Content Relation

Hysteresis in the moisture tension–water content relation of soils, which has often been observed, has generally been regarded as associated with delay in the refilling of empty parts of the pore space upon wetting (Haines, 1930, and Smith, 1936). Other theories of hysteresis as observed in adsorption phenomena (Foster, 1951, and others) also require the presence of both air (or vapour) and liquid in the pore space. Therefore although differing in the mechanisms postulated, all are alike in considering that it is the occlusion of air in parts of the pore space which is a necessary accompaniment of a lower water content for a given moisture tension upon rewetting. This effect is demonstrated here by the lowered degree of saturation for a given water content when the clay blocks are wetting as compared to drying out.

But in the case of the clay blocks here considered this lower degree of saturation can account for only a small part of the difference in water content between the two branches of the pF-water content curves. Curve 4 in Fig. 2 and curve 3, Fig. 3, represent the wetting branches when the water contents of the blocks are corrected by the increment necessary to make the degree of saturation the same as for the drying-out curves. It is clear that most of the horizontal distance between the two experimental curves is the result of a difference in volume of the pore space of the blocks. The blocks on rewetting from pF 6·0 have failed to regain the original volume which they had at a given moisture tension.

This failure of the blocks to regain their original volume continued to the end of the rewetting curve at pF 2·0. For this reason a third branch of the pF-water content curve was obtained with some red clay blocks which had first been reduced in volume to the minimum at pF 6·0 and then rewetted to pF 2·0. This is shown by curve 3 of Fig. 2. The horizontal distance between the two original branches has been reduced approximately by the amount by which the loop failed to close at pF 2·0. It appears likely that this last branch and the wetting branch constitute a reproducible hysteresis loop (Croney and Coleman, 1954) which should

be the same if the blocks were taken repeatedly through a wetting and drying cycle. Countless seasonal cycles of this kind, although of diminished severity of drying, have of course been experienced by the undisturbed soil and natural aggregates of the red clay, and these were examined to see whether they would give the same reproducible loop.

The pF-water content relation of these aggregates is shown in Fig. 4. The loop closes at both ends, but the natural variability of the aggregates makes precise measurements impossible. Curve 3 in Fig. 4 gives the wetting branch for the red clay blocks (taken from Fig. 2) which closes fairly accurately with the ends of the loop for the aggregates.

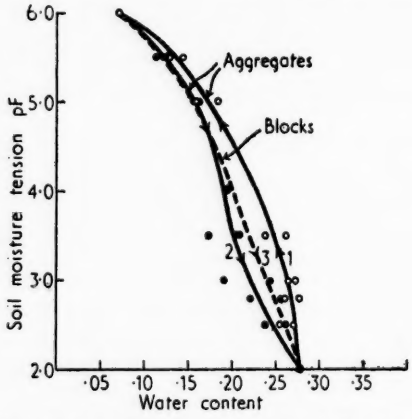

FIG. 4. Comparison of moisture-tension relation for moulded blocks and natural aggregates.

Schofield (1935) suggested that hysteresis in soil moisture tension–water content of systems containing clay-size particles may be associated with plastic readjustments of the clay particles, relative to each other. Barkas (1946) has elaborated a similar idea and claims his theory has general applicability to swelling substances, although in developing it he was interested in wood gel substance. The consolidation test in soil mechanics demonstrates a very similar kind of hysteresis. According to these ideas hysteresis should be expected in water sorption phenomena, whenever uptake of water is associated with swelling and enlargement of the pore space. It is the result of plastic readjustments of the clay particles; the area of the loop represents the energy lost per cycle by the clay-water system.

Comparison of the Moulded Blocks and the Undisturbed Clay

Lauritzen (1948) has shown in much detail how the apparent swelling behaviour of blocks and clods is different if the outside dimension of the sample be used as the measure of volume change. But the correspondence of the moisture tension–water content relation of the red clay blocks and red clay aggregates, shown in Fig. 4, suggests that the water

is held in essentially the same way both in blocks and aggregates, within the measured limits of soil moisture tension.

The degree of saturation of the red clay in the field is known from density measurements. It is 0·93 at a water content of 0·29 g./g. which compares with 1·0 for the red clay blocks at a similar water content. The natural clay, therefore, possesses a greater porosity than the moulded block for a given water content. But the data of Fig. 4 suggest that the swelling behaviour of the aggregate is very similar to that of the moulded block, which may be regarded as an aggregate from which the large structural pores have been removed. An important consequence of this would be that apart from these few large pores the red clay aggregate would remain pore space saturated until dried to pF 5·0.

Summary

The sorption of water by moulded clay blocks was examined in the moisture tension range from pF 6·0 to pF 2·0. Change in volume of the pore space (i.e. swelling) was more important than filling or emptying of the pore space by water, in determining the total water uptake between these limits. In fact, between pF 2·0 and approximately pF 5·0 all water content change was accompanied by an equal change in volume of the pore space if a small hysteresis in wetting is neglected.

The moisture tension–water content relation of some natural clay aggregates was very similar to that of the blocks made from the same material. This suggests that the water is held both in moulded blocks and natural aggregates in essentially the same way within the range pF 2·0 to 6·0, and that the moisture tension–water content relation in the case of this clay is determined by the swelling property of the clay rather than by pore-size distribution.

The hysteresis in the moisture tension–water content relation of the clay blocks cannot be accounted for, solely, by the effect of delay in refilling empty parts of the pore space, on rewetting. Most of the hysteresis appears to be associated with plastic readjustments of clay particles relative to their neighbours.

Acknowledgements

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COARSE PARTICLE DISTRIBUTION IN THE SKELETON OF SOME COARSE- TO MEDIUM-TEXTURED SOILS[1]

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Abstract

In New England many of the soils are predominantly sandy and gravelly. Because of the intensive agriculture practised, costing as much as $2,000 per acre to produce some crops, obtaining quantitative data on the content and distribution of coarse particles in the profiles of these soils is useful in predicting their behaviour in the growing of highly specialized crops. For example, the highest quality cigar tobacco is grown on the coarser-textured soils. A quantitative study of the coarse particles in ten profiles each of the Hinckley and Merrimac series and four profiles each of the Cheshire and Enfield series has been made. The Hinckley was outstanding in containing more than 60 per cent. gravel in the D_1; the Merrimac was intermediate with 25 per cent. in the D_2; the Cheshire and Enfield next in order with about 20 per cent. in the substratum. For the Cheshire and Enfield soils, the gravel content was about 2 per cent. greater in the A_p horizon of the cultivated soil than in the forested counterpart. Organic matter losses and compaction decreased their total porosity 25 per cent. These factors plus removal of stones for cultivation are thought to account for about one-half of the reduction in thickness of the solum; the remainder probably is due to soil removal by erosion.

In New England many of the soils are predominantly sandy and gravelly while some are medium-textured with an admixture of gravel. Another common characteristic is a low clay content of <15 per cent. (Swanson *et al.*, 1952). In the Connecticut Valley many of the coarser-textured soils are used for growing intensive crops like tobacco and vegetables. Production of these crops requires high investments per acre. Although soils high in sand and gravel would be of little importance in most areas because of their droughtiness and general lack of fertility, they are of special importance in the Connecticut Valley because of their adaptability to the growing of these intensive crops. According to Anderson (1953) the highest quality tobacco is produced on the coarser-textured soils. These kinds of soils warm up earlier in the spring, making possible the production of early vegetables.

Since these soils are naturally infertile, fertilizers must be applied if crops are to be produced successfully. This deficiency in fertility is corrected in tobacco growing by applying as much as 200 lb. N, 120 lb. P_2O_5, and 200 lb. K_2O per acre annually. In dry seasons the droughtiness of these soils is corrected by irrigation. With irrigation becoming more prevalent each year, the physical nature of soils becomes more important. Some of these soils, however, are more gravelly and droughty than others,

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[2] Chief Soil Scientist and Research Assistant in Soils, The Connecticut Agricultural Experiment Station; and formerly Graduate Student, Yale University, New Haven, Conn., respectively. Grateful acknowledgement is made to A. E. Shearin for his assistance in locating the sample sites and writing the profile descriptions and to D. B. Downs, J. Friedman, and M. Wang for assistance in the field and laboratory work.

resulting in increased irrigation and subsequent leaching of plant nutrients, especially N and K_2O (Anderson *et al.*, 1932).

In making the soil survey of Hartford County, Connecticut, the intensive nature of the agriculture is taken into account in classifying and mapping the soils. Because of the generally sandy and gravelly nature and intensive use of the soils, laboratory and field studies have been made to ascertain how much emphasis should be placed on sand and gravel in the classification and mapping of these soils. Some of the results of these studies are presented here.

On a qualitative basis, the Hinckley contains large amounts of gravel and may be considered a skeletal soil, the Merrimac has considerably less gravel than the Hinckley throughout the profile, and the Cheshire and Enfield differ in their distribution of gravel in the profile. This paper reports on a quantitative study of the gravel fractions of ten profiles each of the Hinckley and Merrimac series and four profiles each of the Cheshire and Enfield series.

General Description of the Soils

The profiles sampled are all located in Hartford County, Connecticut. All soils are well-drained members of the brown podzolic great soil group. On the basis of field studies, the profiles sampled are believed to be representative of the respective soils. Additional information on the physiography, geology, climate, and vegetation of the area in which these soils occur is given elsewhere (Swanson *et al.*, 1952).

The Hinckley and Merrimac soils are developed on glaciofluvial deposits. The Merrimac soils are found on terraces and plains of Late Wisconsin glacial drift; the Hinckley soils are generally found on kames and eskers. Flint (1953) has suggested the drift to be of Cary age. The soils are developed over stratified sands and gravels derived principally from granite, gneiss, or schist. In general, the Merrimac samples were taken on slopes of 0 to 3 per cent. and the Hinckley on 3 to 15 per cent. Detailed descriptions of the profiles sampled are given elsewhere (Swanson and Ritchie, 1954).

A large percentage of the Merrimac soils is cleared and used mainly for tobacco, potatoes, vegetables, and corn production. The Hinckley soils are not cleared and farmed as intensively as the Merrimac. Many of the cleared areas of the Hinckley are idle or in hay or pasture, but some are used for tobacco and, to a lesser extent, vegetables where they are closely associated with the Merrimac and other more productive soils.

The Enfield and Cheshire soils are found on Late Wisconsin till. The Enfield[1] soils are developed from eolian deposits, which lie over the coarse sandy, very firm till of the Cary substage (Flint, 1953) of the Late Wisconsin drift sheet. The till is derived mainly from acid reddish-coloured Triassic sandstone, arkose, and conglomerate. The contact between the eolian deposit and the till is not always sharply defined. The Cheshire soils, however, are derived directly from tills

[1] These soils are developed over coarse-textured till and were formerly included in the Enfield series. In the Hartford County survey, they are separated from the Enfield soils over stratified sand and gravel. The name Enfield is tentative pending correlation.

similar to those underlying the eolian deposit. Weathering has penetrated in both soils to about 24 in., but there is little indication of weathering of the till. They are on ground moraines with slopes ranging from 1 to 4 per cent. A soil survey of the Scantic River Watershed (Montgomery, 1939) showed that Enfield was the most erosive soil in this watershed. Large acreages of potatoes and tobacco are grown, especially on the Enfield.

Two sampling sites each for both the Enfield and Cheshire soils were selected in representative areas where cultivated fields are adjacent to forests. Profiles were sampled from each cultivated and forested site for the study of the differences associated with the farming of these soils. The Enfield soil at the Manchester site is known to have been in cultivation for about 80 years. It is not known how long the other cultivated fields have been farmed. Photographs of a Cheshire and an Enfield profile under forest cover are shown in Plates 1 and 2, respectively.

Profile descriptions of one of the Cheshire fine sandy loam sites and one of the Enfield very fine sandy loam sites, the predominant types sampled in these series, are given below.

Cheshire Fine Sandy Loam

Sample No. S51 Conn. 2–2–(1–6), Hartford County, Conn.

Location: Town[1] of Manchester; 0·8 miles north of village of Buckland. Samples taken in forested area on Hartman Tobacco Farm. Co-ordinates on Soils Department C.A.E.S. soil profile location map (Manchester U.S.G.S. quadrangle): No. 10, 5–D.5, 375.

Vegetation: Forest; mainly black and white oak with little red oak, some beech and white pine.

Topography: Undulating ground moraine; 2–3 per cent. slope; elevation about 280 ft.; general area undulating to hilly.

Drainage: Well drained. Surface run-off is high. Rapid to moderately slow permeability. (Soil Survey Staff, p. 167.)

Parent Material: Generally acid reddish-coloured Triassic materials principally of sandstone, arkose, and conglomerate, with some shale and siltstone.

Soil Profile Description

Horizon	*Depth*	*Description*
A_0*	½ to 0 in.	Well-decomposed leaf litter. Mull humus type.
A_1	0 to ½ in.	Very dark greyish-brown (10 YR 3/2)[3]—fine sandy loam, very friable; loose and fluffy. Very thin *Bleicherde* at base of this horizon; pH 3·5.
A_p	½ to 6 in.	Dark brown (7·5 YR 4/4) fine sandy loam or loam; very friable, very weak subangular blocky; some gritty material present. Lower boundary not distinct; pH 3·8. Rapid permeability.

[1] Towns in New England are the counterpart of townships, school election districts, and the like in other regions.

* In Connecticut it is not unusual to find very thin A_0 and A_1 horizons in areas previously cultivated, probably 75 to 100 years or more ago (as estimated from present tree growth), and now in forest. Since the first settlement in Connecticut in 1633 at Windsor in Hartford County, the land has been cleared, farmed, abandoned, and new forest growth appeared, many places probably going through one or more complete cycles. The plough layer is discernable because of the darker colour of the soil compared with the B. In many places, the A_p is easily discernable, but in others, it is not so easily seen.

[3] Munsell color notations on moist soil (Soil Survey Staff, 1951).

B_{21}	6 to 14 in.	Yellowish-red (5 YR 4/8) fine sandy loam or loam; very friable; weak medium subangular blocky; small amount of gritty material and small rock fragments; grades into underlying horizon; pH 4·0. Rapid permeability.
B_{22}	14 to 18 in.	Dark red (2·5 YR 3/6) sandy loam; friable; weak medium subangular blocky; gritty material and small rock fragments fairly numerous. Lower boundary distinct; pH 4·0. Moderately rapid permeability.
C	18 to 26 in.	Dark red (10 R 3/6) gritty till of coarse sandy loam texture, derived mainly from reddish conglomerate, sandstone, and arkose. Very firm in place and hard when dry; moderately firm and friable when moist; fine pinholes numerous; rocks and rock fragments are mainly conglomerate, sandstone, arkose, and gneiss and rounded quartz. Roots are well distributed in solum but practically none in till; pH 4·1. Moderately slow permeability.

Enfield Very Fine Sandy Loam (Over Till)

Sample No. S51 Conn. 2–1–(1–6), Hartford County, Conn.

Location: Town of Manchester; 0·6 miles north of village of Buckland; about ⅛ mile south-west of the Cheshire site. Samples taken in forested area on Hartman Tobacco Farm. Coordinates on Soils Department C.A.E.S. soil profile location map (Manchester U.S.G.S. quadrangle); No. 9, 5–D.5, 65V.

Vegetation: Forest; mainly black, white, and red oaks, red maple, with some beech, chestnut sprouts, and a few white pine.

Topography: Gently sloping area of about 3 per cent. grade on same ground moraine as Cheshire site; elevation about 240 ft.; general area undulating to hilly.

Drainage: Well drained. Surface run-off is medium to high. Moderately rapid to moderately slow permeability.

Parent Material: Eolian deposits overlying coarse-textured very firm or compact till consisting of generally acid reddish-coloured Triassic sandstone, arkose, and conglomerate.

Soil Profile Description

Horizon	*Depth*	*Description*
A_0	½ to 0 in.	Well-decomposed leaf litter. Mull humus type.
A_1	0 to ½ in.	Very dark greyish-brown (10 YR 3/2) very fine sandy loam; very friable, loose and fluffy. Very thin *Bleicherde*—0·1 in. thick at base of this horizon; pH 4·2.
A_p	½ to 6 in.	Dark brown (7·5 YR 4/4) very fine sandy loam; weak medium crumb; very friable; fine and medium roots well distributed. Lower boundary not distinct; pH 4·4. Moderately rapid permeability.
B_{21}	6 to 16 in.	Strong brown (7·5 YR 5/8) to yellowish-red (5 YR 4/8) very fine sandy loam; very friable; weak medium subangular blocky; a few medium and coarse sand grains and small rock fragments are present. Lower boundary not distinct; pH 4·6. Moderately rapid permeability.
B_{22}	16 to 24 in.	Colour and texture the same as the overlying horizon; gritty material and small rock fragments are more numerous, which is the principal difference. Lower boundary fairly distinct; pH 4·8. Moderate permeability.

D 24 to 36 in. Dark reddish-brown (5 YR 3/4) coarse sandy loam or loamy coarse sand till, derived mainly from reddish conglomerate, sandstone, and arkose. Very firm in place and hard when dry; moderately firm and friable when moist; fine pinholes numerous; breaks into irregular fragments when dry—no roots in this horizon; pH 5·4. Moderately slow permeability.

Collection of Samples

One-eighth cubic foot boxes (6 × 6 × 6 in.) made of 20-gauge galvanized sheet iron were used for obtaining samples of uniform volume for the Hinckley and Merrimac soils. Samples were taken at 6-in. intervals to 3 ft. in these coarser-textured soils, for it is difficult to distinguish accurately between horizons. In sampling the Cheshire and Enfield soils, it was found that samples could be taken more easily and more representative samples obtained using a larger box of ½ cu. ft. volume (12 × 12 × 6 in.). Duplicate samples were collected about 6 ft. apart in each genetic horizon. After driving the boxes into the soil, the soil adjacent to the sides of the box was removed, spades were driven under the box, the sample lifted out and trimmed flush with the edges of the container. The samples were placed in cloth bags, weighed in the field, and taken to the laboratory for analysis.

The authors realize that it is impossible to take samples of uniform volume of gravelly soils. The sampling, however, was done under similar conditions, and reasonably uniform unit volumes were obtained.

Laboratory Procedures

The samples were oven-dried to constant weight, then placed in a nest of 8-in. diameter, round-holed sieves and shaken for 15 min. in a Tyler automatic 'Ro-Tap' sieve-shaking apparatus having a circular horizontal motion (Krumbein and Pettijohn, 1938). The results are calculated as percentages based on the oven-dry weight of the whole sample (gravel >2 mm. + soil <2 mm.). The sieve diameters used were 3, 2, 1, and 0·5 in. and 5 and 2 mm. In the Hinckley and Merrimac the 3-in. sieve was omitted. The 3 to 0·5-in. sieves were round-hole brass stone sieves of A.S.T.M. specification E-11. Brass round-hole plate type sieves were used for the remaining smaller sizes. The entire soil sample was sieved in portions small enough to prevent clogging of the sieves. Any 5 and 2 mm. fractions retained as aggregates were crushed by hand and the screens shaken again for several minutes, then washed free of silt and clay, sieved in water, oven-dried, and weighed.

The >2 mm. material in mechanical-analyses determinations are usually not included in the results or are reported only as a percentage of the air-dry weight of the whole sample (Kilmer and Alexander, 1949). Since for the purposes of this study it was believed that the size ranges set for gravel separates[1] were too broad, the fine-gravel and gravel separates were each separated into coarse and fine fractions. Geologists use several grade scales, but none of these scales was found to be suitable,

[1] Soil Survey Division, U.S.D.A. Progress Report of Committee on Soil Texture, 18 Oct. 1949. In this paper, for convenience of discussion, the cobble fraction will be considered as part of the gravel fraction.

for the size ranges did not fit the categories mentioned above. These sieve separations represent the following separates as based on the U.S. Department of Agriculture standards (Soil Survey Staff, 1951).

1. 3 in.+	cobbles
2. 3–2 in.	coarse gravel
3. 2–1 in.	gravel (coarse fraction)
4. 1–0·5 in.	gravel (fine fraction)
5. 0·5 in.–5 mm.	fine gravel (coarse fraction)
6. 5–2 mm.	fine gravel (fine fraction)

Results and Discussion

Results from the sieve analyses are presented in Fig. 1 as average values. The data are plotted on probit log paper, a method of plotting data devised by Bliss (1935) for smoothing curved lines, which serves as an aid to interpreting the data.

Of the soils studied, the Hinckley was outstanding in containing the most gravel in the profile, the Merrimac was intermediate, with the Cheshire and Enfield next in order. In the Hinckley D_1 12–18 in. horizon more than 60 per cent. of the soil was composed of gravel; of this amount about 25 per cent. consisted of gravel >2 in. For the other soils, only in the Merrimac D_1 and D_2 and the Enfield D (cultivated) did the coarse fragments comprise 25 per cent. of the soil material. For all the other horizons the amount was less than 20 per cent.

The Hinckley contains less fine-textured material intermingled with the gravel than the Merrimac, causing the Hinckley to be more droughty. As might be expected from the soil textural classes, field observations show the Cheshire fine sandy loam and Enfield very fine sandy loam soils to have good moisture-holding qualities. The better moisture relationship in these two soils is also reflected in the lower coarse fragment content of the profiles.

The Hinckley contained the highest amount of gravel, 22·7 per cent., in the surface horizons of the soils studied. Although the Merrimac is usually thought to be quite gravelly, this soil had the lowest amount, 2·6 per cent., of gravel in the surface horizons. Only the 5- and 2-mm. sizes were found in the Merrimac, while in the Hinckley the >2 in. size alone comprised 3·5 per cent. of the gravel. The Cheshire and Enfield, which contained the next largest amounts of coarse materials actually had smaller amounts of 5- and 2-mm. particles than the Merrimac. The separates >5 mm. accounted for the high amounts of coarse fragments in the surface horizons of the Cheshire and Enfield.

The B horizons show trends in gravel content similar to the surface horizons. The Hinckley is highest with 50 per cent. The gravel in the Merrimac B increases with depth, especially in containing more of the larger sizes. In the Enfield profile description given above, the principal difference noted in the field between the B_{21} and the B_{22} was the higher coarse fragment content. Analyses of these fragments showed 11·2 and 16·8 per cent. for these respective horizons. The differences between the Cheshire and Enfield B horizons are small, although the forested

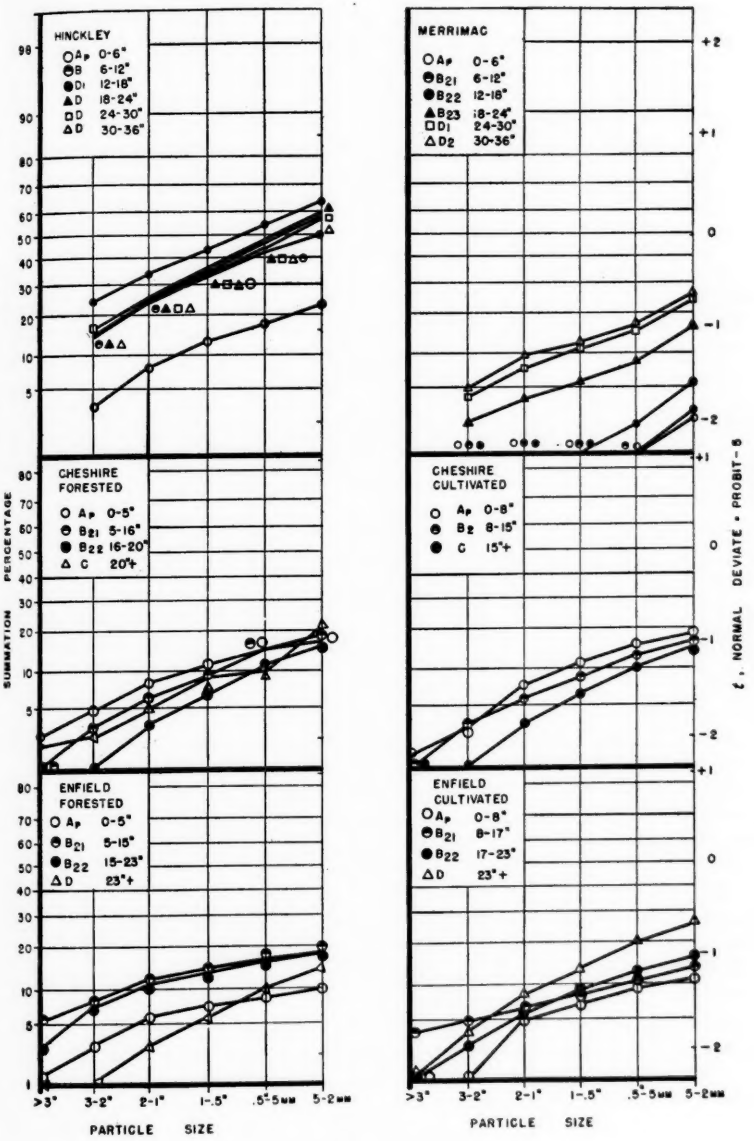
HINCKLEY
MERRIMAC
CHESHIRE FORESTED
CHESHIRE CULTIVATED
ENFIELD FORESTED
ENFIELD CULTIVATED
SUMMATION PERCENTAGE
PROBIT - 8 • NORMAL DEVIATE
>3" 3-2" 2-1" 1-.5" .5-.5MM 5-2MM
PARTICLE SIZE

FIG. 1.

profiles of each soil have slightly higher amounts of gravel than their cultivated counterparts. It is possible that removal of the protective forest cover has resulted in more freezing and thawing, heaving the coarse fragments toward the surface in cultivated soils. Since the Enfield solum is dominantly of eolian origin, frost action, tree overthrow, and earthworm and rodent activity may account for the mixing of till fragments with eolian materials in the solum.

Unpublished data (Doehne, 1952) show the effects of gravel on the permeability rates in soils. The highest rate for the Merrimac, 33 in. per hour, occurred in the D_2, which also had the highest gravel content. For the Cheshire, the highest permeability, 9 in. per hour, occurred in the A_p (forested), the horizon with the greatest amount of the larger gravel particles. However, in the finer-textured Enfield (forested), which contained less gravel than any of the other soils, permeability was influenced more by organic matter than by gravel. The permeability rate of 3 in. per hour for the B_{21} was lower than the 13 in. per hour in the A_p. The A_p horizon for this soil contained, on a percentage basis, about 18 per cent. less gravel than the B_{21}. Other factors, such as porosity, may have been the limiting factor in permeability rates. In the Cheshire, the non-capillary porosity was 12 and 10 per cent. in the A_p and the B_{21}, respectively. For the Enfield, the values were 14 and 8 per cent., respectively.

The effect of coarse materials on loss of soil by erosion may be shown by comparing the forested and cultivated profiles of the Cheshire and Enfield. From field observations, it is known that the Cheshire is less erosive than the Enfield. The surface of the former soil contains about 17 (forested) to 19 per cent. (cultivated) gravel (Fig. 1) and the latter about 9 to 11 per cent. Also the Cheshire contains slightly more of the larger gravel sizes in the surface than the Enfield and has the greatest amount of gravel in the lowest horizon. The effect of increased amounts of gravel on increasing the permeability as mentioned above is reflected in the erodibility of the soil. Apparently, there has been little erosion on this cultivated soil. The amount of soil lost by erosion has not greatly increased the concentration of gravel in the surface as noted in the average percentage differences of 2 per cent. between the forested and cultivated soils. It is doubtful if these differences are great enough to be distinguished visually and used as an aid in mapping erosion on these soils. Observations indicate that in areas of considerable erosion gravel accumulates on the surface (Baur and Adams, 1953).

In New England stones, cobbles, and the larger gravel fragments are picked off the cultivated fields each spring. The effect which this practice has had on the amount of coarse fragments remaining in the surface horizons can be seen by comparing the forested with the cultivated soils. The Cheshire forested soil, on a percentage basis, contains about 2 per cent. more gravel >2 in. than the cultivated; for the Enfield this was about 3 per cent. Both these soils, especially the Cheshire, contain appreciable amounts of stones and cobbles and are mapped with varying degrees of stoniness. Stone walls containing the larger stones have been built. Gravel fragments <2 in. are not picked off the land, for the

obvious reason that they do not interfere with cultural operations as seriously as the larger fragments.

The practice of removing coarse fragments each spring from the surface may account, in part, for the decreased depth of solum of cultivated soils in comparison with forested ones; the sola of the forested sites were about 2 to 5 in. deeper than those of the cultivated soils. Judging from the size of the stone walls, 5 per cent. would be a conservative estimate of the volume occupied by stones, cobbles, and gravel removed from the surface. The bulk density of the cultivated soils has increased from 0·9 to 1·3, and their total porosity decreased about 25 per cent., indicating compaction of the cultivated soils. If the volume represented by removal of coarse fragments is added to the decrease in volume of these soils caused by decreased organic matter, or by cultivation, or by tree roots or compaction by tractors, it is likely that as much as a half or more of the reduction in thickness of the solum can be attributed to these factors and the remaining amount to removal of soil by erosion. These quantitative data are helpful in improving qualitative criteria set up for mapping the degree of erosion.

It is a common practice in making chemical investigations on soils and in many of the physical analyses to sieve the soil first through a 2-mm. sieve. Hence, the conclusions drawn from laboratory determinations are based only on soil particles <2 mm. When soils with high gravel contents are compared, or interpretations from physical and chemical analyses are made, particular attention should be given to the effect the coarse fractions may have on soil properties. For example, lysimeter studies (Morgan and Street, 1939) have shown that coarse-textured soils do not retain precipitation as effectively as those low in coarse materials. They are less favourable for crop growing (Anderson *et al.*, 1932), requiring frequent addition of nitrogen throughout the growing season, in addition to requiring irrigation because of their droughtiness.

The value of having information on the amount and distribution of coarse particles in classifying soils is shown by the Hinckley and Merrimac soils. Some years ago a question arose as to the need for both the Hinckley and Merrimac series since they were similar in many respects morphologically. It is evident from Fig. 1 that the Hinckley has a higher percentage of coarse fragments than the Merrimac and that this major physical difference would affect the behaviour of these soils in many ways. On the basis of the analyses of the coarse fragments in these two soils and from field observations, these soils have been retained as separate series in Connecticut.

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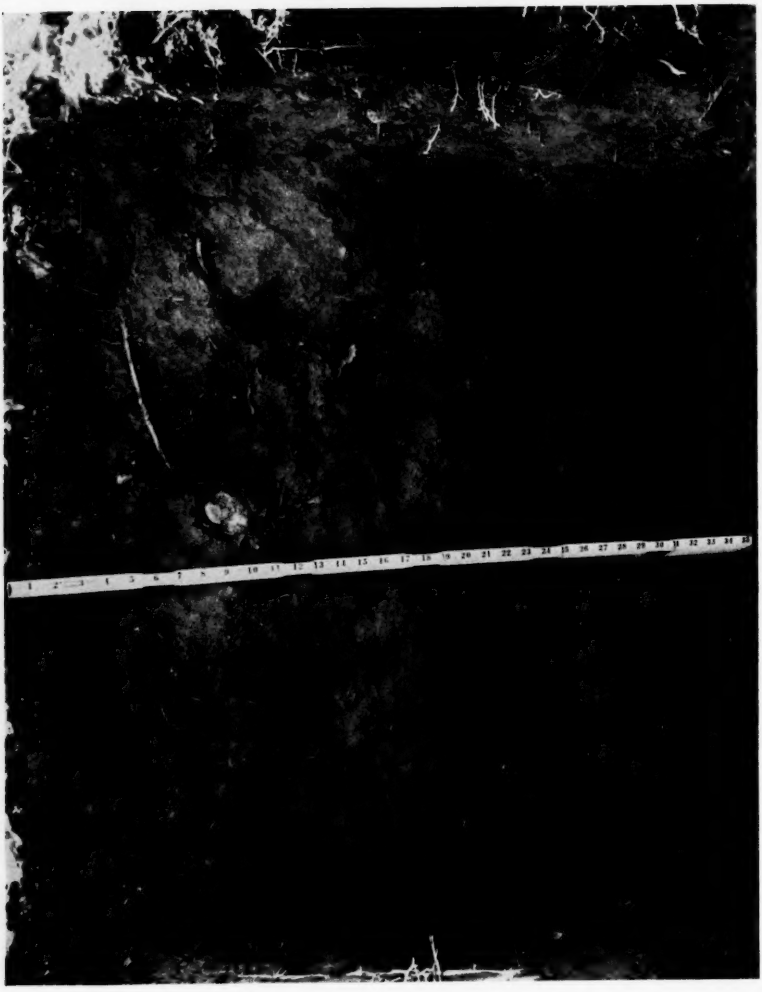
(*Received 11 November 1954*)

Cheshire fine sandy loam developed under forest, Manchester, Conn. A description of this profile is given in the text. The coarse fragments in this soil are admixed with soil materials (< 2 mm.) that are more sandy-textured than in Plate II

C. L. W. SWANSON, A. RITCHIE, JR., AND H. A. DOEHNE—PLATE I



Enfield very fine sandy loam developed under forest, Manchester, Conn. A description of this profile is given in the text. Note the coarse fragments embedded in the finer-textured eolian material

C. L. W. SWANSON. A. RITCHIE, JR., AND H. A. DOEHNE—PLATE II

THE MOBILIZATION OF PHOSPHATE IN WATERLOGGED SOILS

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(Rothamsted Experimental Station, Harpenden)

ALTHOUGH much work has been concerned with the fixation of applied phosphate and the residual value of such phosphate to crops, very little study has been made of the effect of waterlogging on native or added soil phosphates. In view of the role of ferric and aluminium oxides in phosphate fixation, the present study was undertaken as a continuation of previous work on the mobilization of sesquioxides under waterlogged conditions (Bloomfield, 1951). Knowledge of the effect of waterlogging on the mobilization of phosphate is, of course, of particular importance in the growing of rice.

The term 'mobilization' is used here to include the conversion of phosphate into either true solution or colloidal suspension. A waterlogged soil may be defined as one which is essentially reducing in character (Pearsall, 1950). In general, the more organic matter present in the soil, the more rapid the change from oxidizing to reducing conditions on waterlogging. Exceptions are base deficient peats, and soils containing organic matter with a C:N ratio greater than twenty.

The Forms of Phosphate in the Soil

In a recent review on phosphate fixation Wild (1950) has divided the retained phosphate into the following groups, iron and aluminium compounds, calcium and magnesium compounds, compounds with clay minerals, compounds with other inorganic soil constituents, and compounds with organic matter. The first three groups of these are the most important.

The formation of iron and aluminium compounds with phosphate leads to a decrease in the availability of applied phosphates. The replacement of such phosphate, either adsorbed or chemically combined, has received attention. Swenson, Cole, and Sieling (1949), in a study of the replacement of the chemically combined phosphate of iron and aluminium phosphates, found that organic anions, humus, and lignin were able to replace the phosphate in these compounds. The most effective anions were those which form complexes with iron and aluminium. Struthers and Sieling (1950) and Bradley and Sieling (1953) studied the effectiveness of organic anions and sugars in preventing the precipitation of phosphate by iron and aluminium at different pH values; they also found that those most effective in preventing precipitation were the anions and sugars forming stable organometallic complexes.

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is given in the text. Note the coarse fragments embedded in the finer-textured eolian material

The materials used were among those produced in the soil by microbiological action.

The calcium and magnesium compounds formed with phosphates are of importance only in calcareous soils. There is evidence for the formation of di-calcium phosphate and apatite-like minerals (Wild, 1950). Di-calcium and tri-calcium phosphates have been shown to be solubilized by many naturally occurring hydroxy and amino-acids (Johnston, 1952) and by some of the micro-organisms in the rhizosphere of growing plants (Gerretsen, 1948).

The two main mechanisms proposed for the reaction of phosphate with clays are the formation of chemical bonds with lattice ions and by adsorption as gegen ions (Wild, 1950). Haseman, Brown, and Whitt (1950) showed that phosphates could form crystalline minerals on interaction with clays. The minerals so formed were phosphates of the substituted palmerite type and members of the variscite-barrandite-strengite isomorphous series. In their studies on the replacement of fixed phosphate from phosphated clay, Swenson, Cole, and Sieling (1949) found that organic anions replaced the fixed phosphate. Fluoride, when present in a 6:1 ratio to the phosphate, and citrate, were particularly effective in releasing the phosphate.

Although attention has been given to certain inorganic forms of phosphate in the soil, the importance of other types must not be overlooked. The organic forms of phosphorus normally present in the soil are phytin and its lower homologues, and nucleic acids, nucleotides, and nucleoproteins. The production of these forms and their place in the phosphate cycle when waterlogging occurs is very uncertain. The soil microflora and fauna require phosphate in their metabolism, but relatively little is known about the forms of phosphate which these organisms can utilize or of their phosphate turnover. In a review of organic weathering by Russian workers, Jacks (1953) reports the work of Glazoskaya and Bolyshev, who found that algae were very active weathering agents. The value of algal residues as a source of phosphate for oat plants has been evaluated by Fuller and Rogers (1952) using the Neubauer technique. They found that the exact value depended on microbiological rather than chemical factors, but over long periods the phosphate of the algal residues was more available than a similar quantity of phosphorus added as phosphoric acid. The ability of blue-green algae to fix atmospheric nitrogen has also been studied (Singh, 1942; Fogg, 1947; Okuda and Yamaguchi, 1952 *a* and *b*). Singh (1950) has proposed a scheme using this ability to enable the 'Usar' lands in India to be reclaimed. A consideration of the data of Fuller and Rogers (1952) and Singh (1950) shows that the algae return annually a considerable quantity of phosphate to the soil (estimated as equivalent to 2·5 cwt. superphosphate per acre). The great importance of the blue-green algae in maintaining the fertility of the paddy fields may be better appreciated when a fuller knowledge of the phosphate metabolism of these organisms is available.

Experimental

The following materials were used in studying the effect of anaerobically fermenting grass on the release of phosphate:

1. Phosphated aluminium hydroxide.
2. Di-calcium phosphate, silicophosphate, and rock phosphate.
3. Basic ferric phosphate (phosphated ferric hydroxide) and ferric hydroxy-phosphate.
4. Phosphated kaolin and phosphated montmorillonite.

Details of the preparation of these materials are given in the appendix.

The reaction mixtures consisted of 5 g. of dried grass in 300 ml. of water, together with either 0·5 g. aluminium or iron phosphate, 1 g. calcium phosphate, or 3 g. clay. Incubation was at room temperature. 'Wash bottle' reaction vessels of the type previously described were used (Bloomfield, 1951). Mercury traps allowed fermentation gases to escape, the traps being closed with small bungs during sampling. The lower ends of delivery tubes were covered with gauze and samples were expelled by a stream of nitrogen. The vessels were flushed with nitrogen before and after sampling.

The centrifuged samples were evaporated to fuming with mixed nitric, perchloric, and sulphuric acids, the residues digested with dilute hydrochloric acid and diluted to volume.

Aluminium was determined absorptiometrically with 'Aluminon' (Chenery, 1948; Robertson, 1950) and iron as ferrous thioglycollate (Sandell, 1944). Phosphate was estimated as molybdovanadophosphoric acid (Kitson and Mellon, 1949). Calcium and magnesium were determined together by titration with di-sodium ethylenediamine tetracetate with Eriochrome black T indicator (Cheng and Bray, 1951).

Calculation of the Amount Mobilized

The amount of any component in solution was calculated from the concentration, as determined, and the weight of solution in the bottle. The amount removed in each sample was calculated and, by summation, the total amount removed was found. The grand total of the particular component at any time is then equal to the amount in solution plus the total previously removed. The grand total was calculated after each sampling for (1) blank fermentations (water+grass), (2) fermentations with phosphates or clays (water+grass+phosphate material), and (3) water-blanks (water+phosphate material). The total amounts mobilized in water-blanks are multiplied by the appropriate factor to give the results in the same units as for the fermentations. By subtracting (1) from (2) the amount due to the mobilization of phosphate is obtained (if phosphate is removed from solution this value will have a negative sign). By comparing (2)–(1) with (3), the effect of anaerobically fermenting grass solution may be compared with the effect of water alone. The results are expressed in milligramatoms (mga.).

The fermentations were carried out in three groups:

(1) aluminium, calcium, and basic ferric phosphates,
(2) different sized fractions of ferric hydroxy-phosphate,
(3) untreated and phosphated clays.

Blank fermentations were carried out with groups (1) and (3) and appropriate water-blanks with each group.

Results

Aluminium phosphate. The amounts of phosphate mobilized in the fermentation and water-blank are shown in Table 1. The values obtained for the aluminium were extremely low and variable, and are not given. The figures for the fermentation do not indicate any mobilization of the phosphate, the average value of which for the fermentation is less than that of the water-blank. The difference between the two, however, is less than the difference obtained between duplicate blank fermentations. The discrepancy is attributed to the experimental error inherent in carrying out such experiments.

TABLE 1

Phosphate mobilized by fermentation of Grass with Aluminium Phosphate, and in the Corresponding Water-blank

Time in days	*Total phosphate present in mg. atoms/10 g. grass*		*Time in days*	*Total phosphate present in mg. atoms/10 g. grass*	
	Water-blank	*Fermentation*		*Water-blank*	*Fermentation*
2	0·02	−0·02	19	0·10	−0·01
5	..	−0·02	22	0·14	0·02
7	0·06	0·04	26	0·15	0·02
9	0·06	−0·02	40	0·14	0·03
12	0·08	−0·08	47	0·14	0·01
14	0·10	−0·05	50	0·14	0·00
16	0·10	0·00			

Calcium phosphates. The presence of fermenting grass caused extensive mobilization of all forms of calcium phosphate (Table 2). The calcium phosphates are all sensitive to changes in pH, their solubility increasing rapidly as the pH decreases. From semi-quantitative tests with di- and tri-calcium phosphate, Johnston (1952) concluded that some naturally occurring organic acids exhibit a solubilizing effect greater than that to be expected from the pH of their solutions. To find the effect of pH on the solubility of the calcium phosphates used in the fermentations the following experiment was carried out: 1 g. of phosphate and 300 ml. of 0·2 N ammonium acetate, which had previously been adjusted to pH 4, 5, and 6 with 2 N HCl, and to pH 7 with 2 N ammonia, were placed in bottles and shaken end over end for 16 hours. The final pH was determined using a Cambridge pH meter. Portions were centrifuged and aliquots of the clear solution were taken for the determination of the calcium and phosphate concentrations. The results given in Table 3 show that all the forms of calcium phosphate are appreciably

TABLE 2

Final pH Values and Calcium and Phosphate Concentrations of Solutions from Fermentations with Calcium Phosphates, and the Corresponding Concentrations in Ammonium Acetate Buffer

Material	*pH*	*mg. Ca/l.*		*mg. P/l.*	
		Fermentation	*Buffer*	*Fermentation*	*Buffer*
Di-calcium phosphate	5·0	264	574	218	382
Rock phosphate .	4·3	132	350	43·6	110
Silico-phosphate .	5·2	547	790	114	306

soluble at pH 4–5. Since the extent of solution was greater in the buffer solutions, it seems that either equilibrium had not been attained in the fermentations, which, over a period of 50 days is unlikely, or that the discrepancy is due to differences in chemical composition between the buffer and the fermentation products. The latter explanation seems the more probable.

TABLE 3

pH Values, Calcium and Phosphate Concentrations of Calcium Phosphates in Ammonium Acetate Buffers

	pH	*mg.Ca/l.*	*mg.P/l.*	*pH*	*mg.Ca/l.*	*mg.P/l.*
Di-calcium phosphate . .	3·94	792	535	6·06	272	177
	4·79	620	416	7·12	162	104
Rock phosphate . . .	4·00	499	166	5·69	66	6·0
	4·69	204	52·9	7·15	3·5	0·5
Silico-phosphate . . .	4·06	941	410	6·97	277	64·1
	4·88	847	356	7·63	161	72·6

Basic ferric phosphate. The amounts of iron and phosphate mobilized in the fermentation with grass and in the water-blank are given in Fig. 1. This shows that the presence of the fermenting grass leads to the mobilization of a comparatively large amount of both iron and phosphate.

Considering the fermentation curves, it can be seen that before the inception of vigorous fermentation, there is an induction period of some 4–5 days. As in the water-blank, the phosphorus mobilized during the induction period exceeds the amount of iron dissolved, and although at this stage more iron is dissolved in the fermentation than in the corresponding period in the blank, the excess of phosphorus over iron is approximately the same in each case. It is apparent from the results of the blank determinations that the basic ferric phosphate is hydrolysed to some extent, and it seems that the same process occurs during the induction period of the fermentation, together with a certain amount of solution-reduction of the ferric compound, caused by the dried grass (Bloomfield, 1951).

Once fermentation commences, solution and reduction of the ferric iron proceeds rapidly, but nevertheless the phosphorus remains in excess of the iron in solution. The removal from the solid phase of the outer-

most layers, which may be supposed to have adsorbed more phosphate during preparation, would expose a surface less rich in phosphate, and in order to restore equilibrium it is conceivable that some phosphate is absorbed from solution. This probably accounts for the decrease in

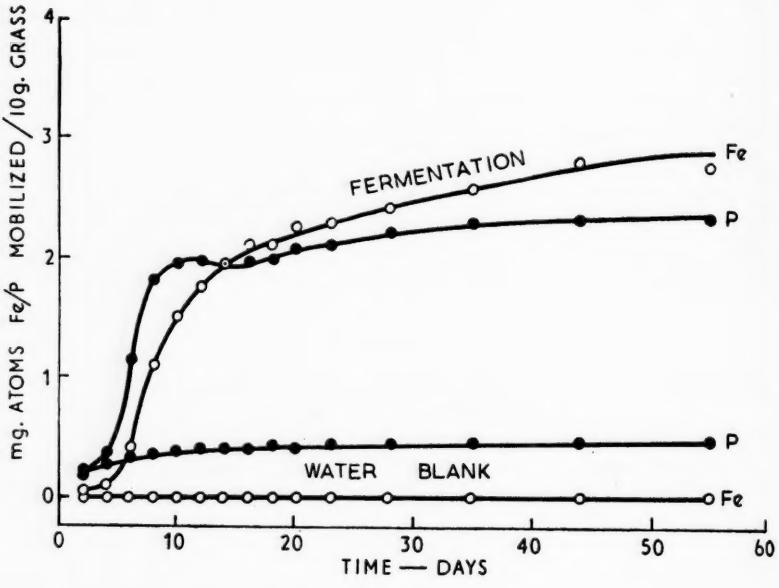

FIG. 1.

total phosphate occurring between 10–20 days from the start of the fermentation (Fig. 1).

Fermentations with ferric hydroxy-phosphate. The ferric hydroxy-phosphate was sieved to yield the following fractions: 40–70 mesh, 70–100 mesh, 100–200 mesh, less than 200 mesh. These different fractions were used in fermentations with grass. The results showed that, as would be expected, the smaller the particle size, i.e. the greater the surface area, the greater the amount mobilized. The results for the fermentations with the fractions 70–100 mesh and less than 200 mesh, are given in Fig. 2. These curves show that in each fermentation the amount of phosphate mobilized is always in excess of the iron. The value of this excess is proportional to the total iron and phosphate in solution and hence to the particle size. Unlike basic ferric phosphate, ferric hydroxy-phosphate gives no appreciable induction period.

It can be seen from Fig. 2 that with ferric hydroxy-phosphate the amount of dissolved phosphorus remains in excess of the dissolved iron throughout the entire reaction. The excess is larger than in the water-blanks, and it seems possible that the previously described phenomenon of sorption of ferrous complexes on the undissolved ferric material may

be responsible for the greater disproportionation (Bloomfield, 1953). Possibly the same process operates with the basic ferric phosphate, but in this case the net effect would vary throughout the reaction because of the concentration gradient of phosphorus in the individual ferric phosphate particles.

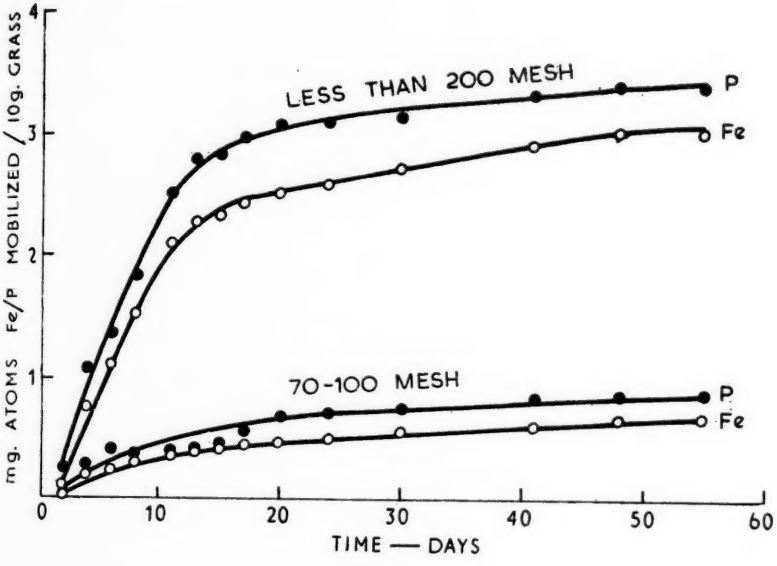

FIG. 2.

Oxidation of solutions from fermentations with ferric hydroxy-phosphate. At the end of the fermentation period the grass was removed by filtration and a few drops of toluene added to each filtrate in order to inhibit further microbiological action. Each solution was placed in a stoppered bottle sufficiently large to be less than half-filled, and the bottles were allowed to stand with occasional shaking. Samples were taken and the pH values and the iron and phosphate concentrations determined. Any precipitate removed was returned to the bottles. The bulk of this precipitate was removed after the penultimate sampling. The results obtained for the solutions from the fermentations with 70–100 mesh and less than 200 mesh material are given in Fig. 3. This shows that equivalently more iron than phosphate was precipitated during oxidation, i.e. the precipitated material was more basic than the original ferric hydroxy-phosphate. Organic matter was co-precipitated with the phosphate and the material varied in colour from dark green-black lustrous material from the coarsest fraction to a light grey-brown powder from the solutions which had mobilized more iron. The comparative stability to atmospheric oxidation of these solutions may be noted; after the initial rapid decrease they retained about 30 mg.

of iron per litre for a period exceeding 4 weeks (in all the references to amounts in the oxidized solution the figures refer to the amount of iron or phosphate present due to the previous mobilization of ferric hydroxy-phosphate. The concentration due to the grass was determined from blank solutions similarly treated and this value was subtracted from the

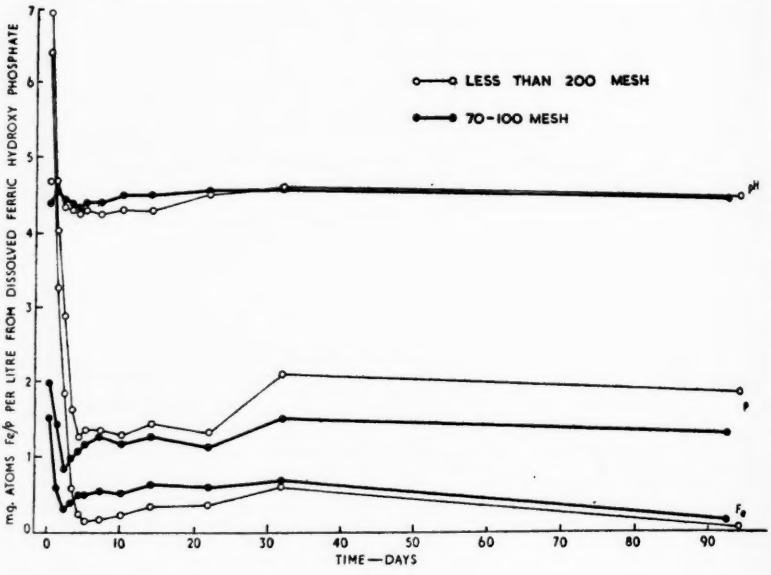

FIG. 3.

concentration as determined in the samples). After 13 weeks the amount remaining in solution is small, amounting to 1–10 mg. iron per litre, but this is still appreciable. The phosphate shows a rapid decrease through the initial precipitation of ferric phosphate, but between 20–30 days an increase in phosphate concentration occurs which is greater than the corresponding increase in iron.

The pH values of the fermented solutions at the start of oxidation were inversely proportional to the amount of iron in solution. The precipitation of iron tended to lower the pH, the oxidation of the solution tended to raise the pH. The result was that the pH fell and then rose again (in the case of the solutions from the two coarsest fractions there was a small initial rise before the decrease). The solutions which had contained least iron showed a net increase in pH during oxidation; the solutions which had contained most iron showed a net decrease in pH during oxidation. The maximum changes in pH during oxidation were of the order of 0·5 pH unit.

Fermentations with untreated and phosphated clays. Fig. 4 shows the results obtained in water-blanks and grass fermentations with phosphated and untreated kaolin and montmorillonite. The results obtained

for water-blanks on untreated clays are not given as the values obtained did not differ from zero by more than the error in reading the Spekker.

Considering the fixation of phosphorus by the untreated clay in the fermentation blanks, it can be seen that for both clays the process appears to be complete in 2 days, the subsequent variation being within the

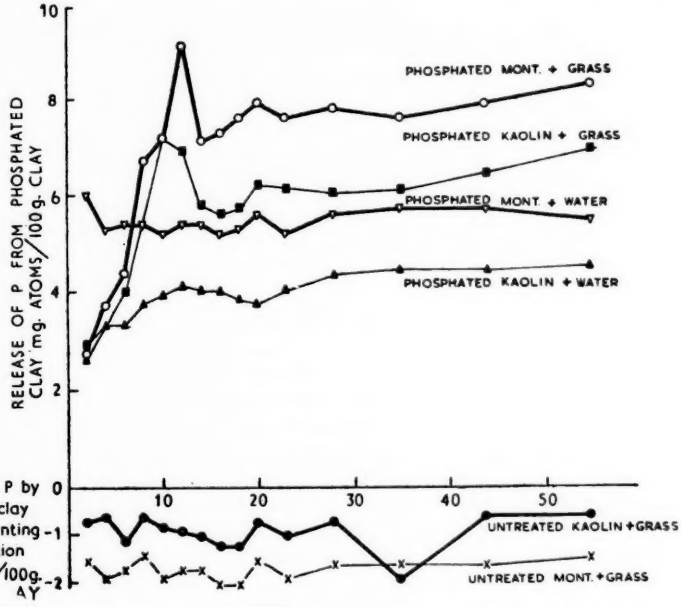
RELEASE OF P FROM PHOSPHATED CLAY mg. ATOMS/100 g. CLAY
PHOSPHATED MONT. + GRASS
PHOSPHATED KAOLIN + GRASS
PHOSPHATED MONT. + WATER
PHOSPHATED KAOLIN + WATER
Fixation of P by untreated clay from fermenting grass solution mg. ATOMS/100g. ΔY
UNTREATED KAOLIN+GRASS
UNTREATED MONT.+GRASS

FIG. 4.

experimental error. The amounts fixed by kaolin and montmorillonite are 0·9 and 1·7 mga. per 100 g. respectively. Whether these figures represent organic or inorganic phosphorus is not known; clays have been shown to fix both types of phosphorus compound (Goring and Bartholomew, 1952; Haseman, Brown, and Whitt, 1950; Wild, 1950).

Considering the release of phosphorus from the phosphated clays, Fig. 4 shows that in the phosphated montmorillonite water-blank, some phosphate was mobilized, and that equilibrium was rapidly established. In the corresponding fermentation there was a rapid release of phosphate followed by a re-adsorption and a second slower release. The total phosphate adsorbed on the clay used in the fermentation was 10 mg. P, and at the end of the experiment the total released was 7·8 mg. P (the maximum value was 8·5 mg. P). In the fermentation with untreated clay 1·5 mg. P were removed from solution. Thus within the limits of experimental error the same amount of phosphate was retained by the clay in each case. The fermenting grass was more effective than water in mobilizing the fixed phosphate. Qualitative observations showed that during the course of the fermentation an appreciable quantity of iron

was brought into solution. This effect may be compared with the results of Goring and Bartholomew (1952) who found that citric-acetic acid treated clays adsorbed less organic phosphorus compounds than the untreated materials, and that this reduction in adsorption was associated with the removal of 'free' iron and aluminium oxides by the acid treatment.

The results for phosphated kaolin show that for the first 4 days the release of phosphate from the clay appears to be due to the water alone, as the values obtained in the presence and absence of grass are the same, within the experimental error. The commencement of vigorous fermentation is accompanied by a large increase in the amount of phosphate released. Some phosphate is then re-adsorbed on the clay and a slow release occurs as the fermentation proceeds. Comparison of the total amount of phosphorus fixed on the clay, the amount released from the clay during fermentation, and that removed by the untreated clay gives the following:

total fixed initially	15 mg. P
total released during fermentation	6·5 mg. P
total removed by untreated clay	0·9 mg. P

These figures show that over half the phosphate initially fixed on the kaolin is not released by the fermenting grass. Wild (1950) presented the two main mechanisms proposed for the reaction of phosphate with clays, as the formation of chemical bonds with lattice ions, and the adsorption as gegen ions. He considers the best evidence for the fixation of phosphate by hydroxyl replacement comes from studies on kaolin. The fixation of the inorganic phosphate by kaolin is believed to take place in two stages. Part of the phosphate is adsorbed by the 'free' sesquioxides on the surface of the clay, and part is fixed by hydroxyl replacement on the aluminium atoms at the edges of the lattice. This may be compared with the two stage process proposed by Haseman, Brown, and Whitt (1950) for the fixation of phosphate by clay minerals, a rapid process followed by a slower. It is considered that the fermenting grass mobilized the adsorbed phosphate, but is unable to release that attached to the lattice aluminium. The stability of aluminium phosphate to the action of fermenting grass lends weight to this latter supposition.

General Discussion

Flood fallowing of sugar-cane fields, in which the fields are flooded to a depth of 6 in. for at least 6 months, sometimes with the addition of molasses, has been referred to by Paul and DeLong (1949). These authors mention that in a survey of these soils Hardy and Rodrigues (1946) found that the easily soluble phosphate content (Truog method) of these soils increased in the vicinity of the upper surface of the water-table. Hardy and Rodrigues suggested that downward movement of phosphorus has occurred especially in the flood-fallowed soils. These observations may be compared with the results of Glentworth (1947) and Glentworth and Dion (1949), who found that in the gleyed G horizon of poorly drained profiles of soils in north-east Scotland, the

dilute acetic acid soluble phosphate was highest and the total phosphate was lowest. Glentworth and Dion also show that the ratio of readily soluble to total phosphorus is highest in the poorly drained soils. Glentworth (1947) remarks: 'The striking reduction in the amount of the total phosphate and the high readily soluble phosphate in the G horizons of the poorly drained soils is possibly related to the reducing conditions. This points to a loss of phosphate in the ground water from these soils.'

The concordance of these results obtained under different climatic conditions is noteworthy, as is the suggestion of the association of phosphate movement with reducing conditions. The present work shows that phosphate associated with iron is mobilized by anaerobically fermenting plant material. The increase in phosphate soluble in dilute acid and the low total phosphate in the horizon at the top of the water-table may be explained in the following manner. The soil in this horizon is 'wet' and therefore reducing. The A horizon is oxidizing so that little downward movement of any mobilized phosphate will occur from it, but some water-soluble organic matter will be carried into the gleyed horizon. Both iron and phosphate will there be mobilized, some moving down the profile and eventually being lost in the drainage water. The gleyed horizon receives little phosphate from the upper horizons, but as it receives fresh organic matter it will tend to lose iron and phosphate to the lower horizons. This downward movement of organic matter will also tend to release and transport any phosphate adsorbed on the clay.

The results may also be applied to soil conditions in rice growing. Flooding the soil leads to an increase in the phosphorus content of the soil solution, and hence, one would expect, to a proportionate increase in the available phosphate, thus providing an explanation for the efficacy of flood fallowing. However, recent work suggests that other factors may be involved, since Keresztény (1953) found that phosphorus liberated in waterlogged soils was not utilized in Neubauer tests.

Summary

The effect of anaerobically fermenting plant material on the mobilization of aluminium, calcium, and iron phosphates, untreated and phosphated clays has been studied. The results obtained were—

Aluminium phosphate: no evidence for the mobilization of either aluminium or phosphate.

Calcium phosphates: extensive mobilization of all forms occurred.

Iron phosphates: two forms of iron phosphate were used, a basic ferric phosphate and a ferric hydroxy-phosphate. The fermenting grass caused mobilization of iron and phosphate. The basic ferric phosphate exhibited re-adsorption of phosphate.

Clays: both kaolin and montmorillonite removed phosphate from fermenting grass solution. With the phosphated clays, fermenting grass mobilized phosphate which had previously been 'fixed'. The amount of phosphate released from the phosphated kaolin was about half of that which had been fixed. For phosphated montmorillonite, the amount

remaining fixed was equal to the amount removed from fermented grass solution by untreated montmorillonite.

Oxidation of the fermentation solutions containing iron and phosphate gave a precipitate of basic ferric phosphate together with organic matter. Small but significant amounts of iron and phosphate remained in solution. It is considered that this stability of mobilized iron phosphate accounts for the movement of phosphate in association with iron within the soil profile.

The results are applied to explain previously reported effects in gleyed and flood-fallowed soils.

Acknowledgements

One of us (J. K. R. G.) wishes to thank the Colonial office for a Training Studentship during the tenure of which this work was carried out. Thanks are due to many people at Rothamsted, but particularly to Dr. A. Muir, and Dr. G. W. Cooke for helpful discussion and encouragement. This paper is based on work presented by one of us (J. K. R. G.) in a thesis in partial fulfilment of the requirements for the degree of M.Sc. in the University of London.

APPENDIX

Materials used in the Fermentation Experiments

Aluminium phosphate (phosphated aluminium hydroxide)

Aluminium phosphate was prepared by first precipitating aluminium hydroxide from potash alum with ammonia. Di-ammonium hydrogen phosphate was added, and the suspension adjusted to pH 4 with phosphoric acid. The resultant product was washed free of phosphate with water, and dried by washing with alcohol and benzene. The benzene was removed by air-drying at 40° C. The final product was a free-running white powder; this was lightly ground in an agate mortar.

Calcium phosphates

Three water-insoluble forms of calcium phosphate were used, dicalcium phosphate, silicophosphate, and ground rock phosphate. The samples were taken from material used in field experiments and were commercial products. They were sieved to pass 100 mesh.

Iron phosphates

Two iron phosphates were used, which were designated basic ferric phosphate and ferric hydroxy-phosphate.

(*a*) *Basic ferric phosphate.* This material was prepared in a manner analogous to the aluminium phosphate. Ferric hydroxide was prepared from ferric chloride, washed until salt-free, and suspended in water. Ammonium phosphate was then added and the suspension adjusted to pH 2·5 by addition of phosphoric acid. The resultant product was washed until phosphate-free, and then dried by washing with alcohol and benzene and drying in air at 40° C. The material produced was an orange-brown powder, which was lightly ground in an agate mortar before use.

(*b*) *Ferric hydroxy-phosphate.* This material was prepared by dissolving ferric chloride in dilute hydrochloric acid, potassium di-hydrogen phosphate in water, and mixing. No precipitate formed. Ammonia was slowly added until the suspension

was at pH 2·5. The precipitate was a light yellow colour and gelatinous. This was washed and dried as previously described. The product, a light yellow powder, was lightly ground in an agate mortar and sieved into different sized fractions.

Clays

Two clay minerals were used, kaolin from St. Austell, Cornwall, and Wyoming bentonite (Upton series). Neither of these materials had been subjected to previous treatment; they were used as received.

Phosphated clays

Samples of the clays were phosphated by the following method: 20 g. of clay was dispersed in 1 litre of a molar solution of KH_2PO_4, heated on a water-bath for 8 hours at 85° C. and then allowed to stand overnight. The clays were washed with water and dried by washing with alcohol followed by air-drying at 40° C.

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SOLUBILITY OF COBALT IN SOIL

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THE essential role of cobalt in ruminant nutrition, and the beneficial effect of this element in correcting certain deficiency diseases of cattle and sheep in many parts of the world, have been fully established for some years. In general, a cobalt content of less than 5 p.p.m. in the soil, or 0·08 p.p.m. in forage, may lead to deficiency diseases (Young, 1948). To counteract the latter, cobalt compounds may be given directly to livestock as additions to their fodder, as salt licks, in drinking water, or in mineral supplements. The element may also be introduced indirectly to animal feeds by the incorporation of a cobalt compound in fertilizers or lime. The latter practice, provided the cobalt addition is sufficient to raise the content of this element in crop or pasture above the minimum requirements for animal health, is obviously a more lasting and effective procedure.

Despite the economic importance of cobalt deficiency, little information appears to be available on the rate of solution of various cobalt compounds when applied to soil. The work described here was designed to obtain some comparative data on the rate of solution of cobalt compounds in soil under natural conditions. Since this rate was measured by periodic determinations of cobalt in rain-water percolating through similar columns of soil, it is actually a resultant of the solubility of cobalt salts under the influence of the chemical and biological agencies in a soil and of the subsequent partial adsorption of the cobalt ion by the soil particle.

Bloomfield (1953), after showing that aqueous leachates of forest litter readily dissolve hydrated ferric and aluminium oxides with the formation of soluble ferrous and aluminium complex compounds, found that sorption of the reaction products takes place concurrently with the solution process and the sorption has the effect of inhibiting further solution of the ferric oxide.

Some interesting work on cobalt in soils has recently been reported by Banerjee, Bray, and Melstead (1953). Using tracer techniques, they found that Co^{60} added to soils was found on extraction to be present in two forms:

1. An easily exchangeable form of cobalt which could be extracted by neutral normal ammonium acetate like other exchangeable bases.
2. A minor fraction consisting of a strongly adsorbed form of cobalt which was not amenable to extraction by (1), but could be removed by leaching with 0·1 N hydrochloric acid under certain pretreatment conditions. This strongly-adsorbed cobalt did not seem to form immediately, but was derived, with the passage of time, from a portion of (1).

Cobalt in the readily exchangeable form of (1) above is held more

strongly in soil than are the other common cations with the exception of hydrogen.

Elgabaly (1950) similarly found that a fraction of the zinc adsorbed by colloidal clays was non-exchangeable with ammonium acetate, and could be considered as fixed by the mineral. He postulated that fixation may be in holes not occupied by aluminium ions in minerals with aluminium in octahedral arrangement, by substitution of zinc for magnesium in those minerals with magnesium in the octahedral position, or by entering the inner layer of the electrical double layer in those minerals in which adsorption of zinc occurs on the surface.

Fuller and McGeorge (1950) reported that only a small amount of the phosphorus added to calcareous soils was securely fixed against extraction with water. There was a distinct relationship between the amount of water-soluble phosphorus and the availability of the phosphorus of the soil to plants.

Experimental Procedure and Results

A quantity of soil from the upper 15 cm. of a sandy clay loam was obtained from uncultivated land near Parkmill in the Gower Peninsula of South Wales, air-dried, and passed through a 10-mesh sieve to remove stones. It was very thoroughly mixed and equal portions equivalent to 500 g. of oven-dry soil were placed in each of eight glass percolating vessels. The soil columns were approximately 50 mm. diameter and 160 mm. long. From the tapered bottom of the percolating vessel a glass tube led the soil solution to a glass storage bottle for periodic determination of cobalt.

The soil was of intermediate texture and, like those of most of Wales, was fundamentally a podzolic type modified by human interference so that the content of organic matter had been raised and the structure improved (Robinson, Hughes, and Roberts, 1950). The soil had a pH of 6·0.

One vessel was carried along as a check, and to the other seven were added a quantity of each of the following cobalt salts equivalent to 0·5 g. cobalt:

cobalt metal, powdered, reduced from oxide,
cobalt carbonate, $Co(OH)_2.4CoCO_3.5H_2O$,
cobalt chloride, $CoCl_2.6H_2O$,
cobalt nitrate, $Co(NO_3)_2.6H_2O$,
cobalt oxide, Co_3O_4,
cobalt phosphate, $Co_3(PO_4)_2.8H_2O$,
cobalt sulphate, $CoSO_4.7H_2O$.

The above substances in finely powdered form, all minus 325 mesh, were spread evenly on top of the percolators and thoroughly mixed with the upper 25 mm. of soil. The air-dry soil was brought to a moisture content equal to half its moisture-holding capacity, with rain-water, and the vessels were placed in an open field exposed to the natural atmospheric conditions, except rainfall, of this locality of South Wales for a period of 270 days.

Since the monthly rainfall in this area may range from under 1 in. to over 6 in., it was decided to eliminate this variable from our study.

The vessels were completely protected from natural rainfall without interfering with other atmospheric agencies of light, air, temperature, &c., and small regular additions of rain-water were made every 3 days to give a uniform rate of 3 in. per 30 days.

The quantity of cobalt added to the soil was greatly in excess of that which would be added in practice to overcome a cobalt deficiency. An application of about 2 lb. of cobalt sulphate per acre applied every 2 or 3 years is usually sufficient to correct cobalt deficiency in the United Kingdom, though in some localities much heavier dressings may be required. The usual minimum cobalt content of soil for the maintenance of health in ruminants, i.e. 5 p.p.m., was increased in this work to 1,000 p.p.m. This was done in order to obtain an accurately measurable quantity of cobalt in the percolated solution, derived from several fairly insoluble cobalt compounds within a reasonable time, without recourse to large lysimeter tanks. The data, therefore, should be viewed solely as a comparison of the behaviour of cobalt compounds, and not as absolute values which would be obtained in practice for economic applications in cobalt-deficient areas.

The chloride, nitrate, and sulphate of cobalt were obvious choices among cobalt compounds, owing to their common occurrence, reasonable cost, and high solubility in water. They are the salts which have been almost invariably used, in experimental work and in practice, on cobalt-deficient areas. Cobalt carbonate and phosphate were included in the test, since additions of cobalt salts are sometimes made to lime, and to superphosphate, respectively, in cobalt-deficient regions. Both the carbonate and the phosphate are nearly insoluble in cold water, and it was desirable to obtain a comparison of their solubility in soil solutions with those of the common soluble cobalt salts which have been utilized in practice. It has been reported by Hill, Toth, and Bear (1953), that applications of liming materials reduced the availability of soil cobalt, a soil of pH 5·8 having twice the cobalt content in alfalfa grown on it of a soil with pH of 7·2. Cobalt metal and oxide are still more insoluble in cold water, but were included in this experiment because nothing has been recorded on their solubility in soil solution and it is conceivable that their lower cost per unit of cobalt and their presumably slower but longer lasting effect might give them advantages under certain conditions.

The solubility of these cobalt compounds was determined solely by the natural effect of rain-water on soil exposed to outside conditions. Since the solubility in practice would depend on the soil, rainfall, and atmospheric conditions which influence the physico-chemical and biological factors governing solubility and adsorption, one can only hope in an experiment of this type to compare the behaviour of various cobalt salts under the interplay of atmospheric agencies and not to give a solubility value which could be applied universally.

It has been shown that minerals with strong attractive forces at the clay surface such as beidellites and illites fixed more potassium than minerals with weaker attractive forces such as montmorillonite. With the same soil, however, the results should reflect the differing behaviour of various salts of cobalt. Similarly, it is known from the work of MacIntyre

and Sterges (1952), that the quantity of soluble silica in a soil may profoundly influence the migrations of various cations in rain-water discharges. Also, the greater the amount of water the greater the downward movement of fertilizer phosphorus (Jordan *et al.*, 1952). McGregor (1953) has shown that the downward movement of total phosphate was appreciable in poorly drained soil, but in a freely drained soil nearly all the applied phosphate was retained in the top 3 or 4 in. of soil. These observations indicate quite clearly that solubility of a cation in a soil depends on the chemical and physical characteristics of the soil, and on the rainfall and atmospheric conditions prevailing at the time.

An important observation in leaching work has been reported by Blume (1952), working with Ca^{45}. It was found that the distance calcium moved from a particular layer was slight, even when the total amount of calcium leached from a soil was appreciable. Apparently calcium moved down the column by a continuous series of displacements, the calcium appearing in the leachates being that originally present in the lower layers of the soil.

In Tables 1 and 2 are presented the data obtained in this experiment. Cobalt was determined in the leachates by the well-known nitroso-R-salt procedure, which is so satisfactory for small quantities of this element (Young, 1953). The higher quantities of cobalt obtained in the first 2 months were checked by the potassium-ferricyanide potentiometric procedure (Young, 1953), and found to be in excellent agreement with the results from smaller aliquots taken for the colorimetric determinations. The mean monthly temperatures for the period are included in Table 1, since the variations in these will obviously have a direct influence on the quantity of cobalt leached from the soil. Such climatic variants, of course, will affect all cobalt salts to the same degree.

In the early period of the experiment cobalt added in the form of nitrate was much more soluble in the soil than cobalt chloride or sulphate. The solubilities in the first month, for instance, roughly approximated the relative solubilities of cobalt nitrate, chloride, and sulphate in cold water. In the next 2 months the rate of solution of cobalt chloride and sulphate was higher than that of nitrate. At the end of the third month the total solubility of cobalt chloride and sulphate was tending to approach that of cobalt nitrate, and at the close of the fourth month the solubilities of cobalt chloride and sulphate, respectively, were 96 per cent. and 86 per cent. of the nitrate. Thereafter, the quantities of cobalt appearing in the leachate from these three soluble salts were small and fairly uniform. At the end of 9 months approximately 85 per cent. of the cobalt nitrate, 83 per cent. of the chloride, and 75 per cent. of the sulphate had been dissolved under these soil and climatic conditions.

Cobalt sulphate appears to be adsorbed by the soil to a slightly greater extent than chloride or nitrate. The quantity of cobalt sulphate appearing in the leachate is somewhat less than can be explained by the difference in solubility between it and cobalt chloride. One would hesitate, however, to ascribe this behaviour to the generalization that adsorption increases with the valency, for this is merely a rough approximation and

actually adsorption is usually specific with regard to both adsorbing substance and the ion adsorbed.

Cobalt in the form of powdered metal, carbonate, oxide, and phosphate dissolved extremely slowly in the soil under these conditions. For the first 3 months cobalt was not detected in the leachates from the jars containing cobalt metal and phosphate, and only traces were found in those derived from carbonate and oxide. Beginning with the fourth month, small quantities of cobalt phosphate became soluble and the quantity of soluble cobalt from the carbonate jar increased. Traces of cobalt were leached from the metal, and very small quantities continued to be rendered soluble from the cobalt oxide. By the end of 6 months the total cobalt rendered soluble by the soil under these conditions was, in percentage of added cobalt, for phosphate 1·94, for carbonate 0·93, for oxide 0·11, and for metal 0·03. Thereafter, small quantities of cobalt continued to be leached from these sparingly soluble substances, the corresponding figures for the cumulative percentage of added cobalt appearing in the leachate at the end of 9 months being for phosphate

TABLE I

Solubility of Cobalt in Soil

Time (days)	*Mean temp. (° F.)*		*Cobalt dissolved*							
			Form of cobalt							
			Check	*Metal*	*Carbonate*	*Chloride*	*Nitrate*	*Oxide*	*Phosphate*	*Sulphate*
30	59·1	mg.	0·54	0·54	0·64	144	307	0·79	0·54	193
		%		Nil	0·02	28·7	61·3	0·05	Nil	38·5
60	53·4	mg.	0·32	0·32	0·44	105·6	89·2	0·44	0·32	130
		%		Nil	0·02	21·1	17·8	0·02	Nil	25·9
90	50·2	mg.	0·20	0·20	0·20	124·0	14·0	0·20	0·20	25·0
		%		Nil	Nil	24·8	2·8	Nil	Nil	5·0
120	48·5	mg.	0·07	0·1	0·7	25·6	6·0	0·18	0·7	10·0
		%		0·01	0·13	5·1	1·1	0·02	0·13	1·99
150	41·0	mg.	0·05	0·12	2·3	6·4	3·2	0·10	6·0	5·6
		%		0·01	0·45	1·27	0·63	0·01	1·19	1·11
180	40·3	mg.	0·06	0·12	1·6	5·6	3·2	0·10	3·1	3·2
		%		0·01	0·31	1·11	0·63	0·01	0·61	0·63
210	45·1	mg.	0·07	0·10	0·40	3·4	3·0	0·19	2·1	3·6
		%		0·01	0·07	0·67	0·59	0·02	0·41	0·71
240	48·5	mg.	0·05	0·15	0·50	1·5	1·3	0·12	2·6	3·0
		%		0·02	0·09	0·29	0·25	0·01	0·51	0·59
270	54·2	mg.	0·07	0·20	0·50	1·00	1·00	0·30	2·90	1·64
		%		0·03	0·09	0·19	0·19	0·05	0·57	0·31

3·43, for carbonate 1·18, for oxide 0·19, and for metal 0·09. It appeared that after the fourth month the soil solution progressively leached out more cobalt from the phosphate than from the carbonate.

Since the readily soluble forms of cobalt chloride, nitrate, and sulphate had virtually reached an equilibrium at the end of 9 months, with only

TABLE 2

Rate of Solubility of Cobalt in Soil

Time (days)	Mean temp. (° F.)	Cumulative percentage of added cobalt appearing in leachate						
		Form of cobalt						
		Metal	Carbonate	Chloride	Nitrate	Oxide	Phosphate	Sulphate
30	59·1	Nil	0·02	28·7	61·3	0·05	Nil	38·5
60	53·4	Nil	0·04	49·8	79·1	0·07	Nil	64·4
90	50·2	Nil	0·04	74·6	81·9	0·07	Nil	69·4
120	48·5	0·01	0·17	79·7	83·0	0·09	0·13	71·4
150	41·0	0·02	0·62	80·97	83·63	0·10	1·33	72·51
180	40·3	0·03	0·93	82·08	84·26	0·11	1·94	73·14
210	45·1	0·04	1·00	82·75	84·85	0·13	2·35	73·85
240	48·5	0·06	1·09	83·04	85·10	0·14	2·86	74·44
270	54·2	0·09	1·18	83·23	85·29	0·19	3·43	74·75

minute quantities appearing in the leachates, it was considered of interest to determine whether the strongly adsorbed residue of cobalt could be removed by leaching with 0·1 N hydrochloric acid as reported by Banerjee, Bray, and Melstead (1953).

The glass vessels were leached on twelve successive days with 50-ml. portions of 0·1 N hydrochloric acid, at the end of which time no cobalt could be detected in the leachate. The leachings were combined and analysed for cobalt by colorimetric, potentiometric, and electrolytic procedures. The results are shown in Table 3.

TABLE 3

Cobalt removed from Soil by 0·1 N Hydrochloric Acid at End of Water Leach Period

	Form of cobalt							
	Check	Metal	Carbonate	Chloride	Nitrate	Oxide	Phosphate	Sulphate
Residual Co in soil before acid leach: mg. Co	..	499·55	494·10	83·85	73·55	499·05	482·85	126·25
% of original added Co	..	99·9	98·8	16·8	14·7	99·8	96·6	25·3
Co extracted by acid leach: mg. Co	0·64	255·73	65·49	79·54	71·81	15·12	403·17	119·42
% of original added Co	..	51·0	13·0	15·8	14·2	2·9	80·5	23·8

Virtually all the cobalt remaining in the soil after the period of 9 months leaching with rain-water was extracted by this dilute hydrochloric acid leach in the case of cobalt chloride, nitrate, and sulphate. These results are similar to those of Banerjee, Bray, and Melstead (1953),

who used neutral normal ammonium acetate for the initial leaching and 0·1 N hydrochloric acid for the final extraction.

The results with the less soluble forms of cobalt, oxide, metal, carbonate, and phosphate were quite different, and, of course, must be considered from the standpoint of acid solubility rather than a strongly adsorbed fraction as in the case of the water-soluble cobalt salts. The dilute acid leach removed very little cobalt from the oxide jar, a fact probably related to the low solubility of cobalt oxides in cold 0·1 N hydrochloric acid solution. The acid treatment brought about half the cobalt metal powder into solution, and this is again undoubtedly related to the inherent solubility of fine cobalt powder in dilute hydrochloric acid under these conditions. The comparatively low solubility of cobalt carbonate in the dilute acid leach was rather unexpected. The total quantity of acid added was greatly in excess of that needed to transform all cobalt carbonate to the chloride. Apparently under these conditions basic cobalt carbonate is not readily soluble in cold dilute hydrochloric acid, or if so, it is immediately adsorbed rather strongly by the soil particle as a basic cobalt chloride. Cobalt phosphate, which had dissolved in 9 months leaching with rain-water to about 3·6 per cent., was brought into solution by the dilute acid extraction to the extent of 80·5 per cent.

Summary and Conclusions

1. The comparative rate of solution of various forms of cobalt in soil under natural conditions in South Wales was determined over a period of 9 months.

2. Cobalt in the form of finely powdered metal, and of oxide, Co_3O_4, dissolved extremely slowly under the atmospheric and soil conditions of the experiment. Less than 0·1 per cent. of the added cobalt in the form of metal, and less than 0·2 per cent. of the oxide were brought into solution in 9 months.

3. Cobalt carbonate or phosphate became slowly available to plants and thus indirectly to animals under the same conditions, the respective solubility values being for carbonate 1·2 per cent. and for phosphate 3·4 per cent. of the original cobalt appearing in the leachates over a period of 9 months. For the first 3 months insignificant quantities of carbonate or phosphate passed into the soil solution, but thereafter small and regular amounts appeared. After the fourth month, the soil solution leached progressively more cobalt from the phosphate than from the carbonate.

4. Cobalt added to soil in the form of chloride, nitrate, and sulphate showed a high rate of solubility. At the end of the first month approximately 61 per cent. of the cobalt applied as nitrate, 39 per cent. as sulphate, and 29 per cent. as chloride had appeared in the leachates. At the end of the fourth month the solubilities had risen to roughly 83 per cent. for nitrate, 71 per cent. for sulphate, and 80 per cent. for chloride. Thereafter, the quantities of cobalt rendered soluble from these salts were small and fairly uniform. It is suggested that cobalt sulphate is more strongly adsorbed by soil than chloride or nitrate.

5. At the end of the 9 months leaching with rain-water under natural

conditions, all soil samples were leached with 0·1 N hydrochloric acid. Practically all the residual cobalt from the cobalt chloride, nitrate, and sulphate samples was extracted by this treatment. The following approximate extractions, in percentage of original cobalt, were obtained from the less soluble forms of cobalt by this dilute hydrochloric acid leach: metal 51, carbonate 13, oxide 3, and phosphate 81.

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VARIATION OF SULPHUR IN SOILS UNDER A CONTINUOUS GRAIN CROP

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THE necessity for the addition of sulphur in one form or another to cultivated soils as a fertilizer has been a matter of controversy, and it is still not at all certain how much importance should be attached to sulphur-containing materials as manures. As far back as 1905, Dymond and his colleagues (1905) reported that for cereal crops and permanent pastures the soil and rain provide all the sulphuric acid necessary. They also stated that a large proportion of other sulphur contained in the soil is rapidly converted into sulphate by microbiological action. As a result of many years experience at Rothamsted, Hall (1905) also held that the rain falling there contributed to the soil enough sulphuric acid to meet the requirements of most crops. This position has been recently approved in America, where in a study of Indiana soils it has been concluded (Bertramson *et al.*, 1950) that 'in general the balance seems to indicate that under average conditions of crop production, the likelihood of sulphur deficiency is not great at present'.

But how far the sulphur content of a soil will change where drainage is free and when known crops are grown does not seem to have been studied. The existence of an area where grain crops have been grown each year for 50 years, and where drainage is very free, at the Woburn Experimental Station gave an opportunity to study the question, seeing that samples of soil have been taken at intervals during the period and were available for examination.

The area in question was under a crop of spring barley every year for the 50-year period 1877 to 1926. The soil of Stackyard Field on which the crop was grown has been described as follows (Crowther, 1936): 'The soils of Stackyard Field . . . are light sandy loams derived from drift over Lower Greensand. Although the surface soils are fairly uniform in texture, the subsoils are much less regular, the predominant material being a reddish brown or yellow sand with irregular patches of somewhat heavier material with lighter colour, or of flint and sandstone gravel cemented with iron oxide. . . . The Lower Greensand contains appreciable amounts of glauconite, particles of which are occasionally found in the soil.'

The soil is easily drained owing to the sandy nature of the subsoil, and there has never been any question of artificial drainage. Even large falls of rain are easily absorbed if the soil is not puddled by heavy cultivation when the soil is wet, so that there is almost always the certainty that any soluble material which is not strongly adsorbed on the soil particles will be quickly removed from the soil. The subsoil is never dry in spite of the fact that there is no water-table within many feet of

the surface. The soil is very deficient in lime, the exchangeable calcium being 7·8 mg.-equivalents per cent. at the time of starting the experiment (Crowther, 1936). At that time the pH value of the soil was 6·1.

The plots with which it is proposed to deal in the present paper are the following.

Plot 1. No addition through the experiment.
Plot 2. Ammonium salts, applied every year. Up to 1906 these consisted of a mixture of ammonium chloride and sulphate; thereafter only ammonium sulphate was used. The application was always in the spring.
Plot 3. Nitrate of soda, applied every year in the spring.
Plot 4. Mineral manures only. Up to 1906 these consisted of a mixture of the sulphates of potassium, sodium, and magnesium with superphosphate: thereafter only sulphate of potassium and superphosphate were used.
Plot 5. Mineral manures as on Plot 4 with ammonium salts as on Plot 2.
Plot 11b. Farmyard manure. The sulphur in the farmyard manure used is not exactly known, but it has been taken as 0·036 per cent. and the sulphur added has been calculated on this basis.

The actual quantities of manures added varied from time to time, but the total amount of sulphur added per acre from this source is shown in the following table.

Plots	S *added per acre per annum 1877–1906*	S *added per acre per annum 1907–26*	*Total* S *added per acre 1877–1906*	*Total* S *added per acre 1907–26*	*Total* S *added per acre 1877–1926*
	lb.	lb.	lb.	lb.	lb.
1	none	none	none	none	none
2	5·9	5·9	177	118	295
3	none	none	none	none	none
4	102·5	48·8	3,075	976	4,051
5	108·4	54·7	3,252	1,094	4,346
11b	6·6	3·3	198	66	264

Even the largest of these figures would not make much difference in the percentage of total sulphur in the soil, when the unit of depth is 9 in., for the weight of soil per acre to this depth is about 1,400 tons.

In addition to the amount of sulphur added in the fertilizers used there will be accretions due to the amount from rain and also that which is directly absorbed from sulphur dioxide in the atmosphere. With regard to the latter the likely amount is not known, though Bertramson *et al.* (1950) state that direct absorption of sulphur by plants has been conclusively demonstrated. Such absorption is, however, probably very small. The soil itself apparently acquires a good deal of sulphur directly from the atmosphere, apart entirely from that from rain and snow. This is actually estimated by Bertramson *et al.* as equal to that obtained from rain and snow, an opinion based on experiments by Alway in Minnesota. The amount from rain and snow is extremely variable, as would be expected. At Rothamsted, from results taken from 1881 to 1887, Hall (1905) gave the amount of sulphur, in the form of sulphates, as 6·96 lb.

per acre per annum. If we can apply this figure to Woburn where the atmospheric conditions were not widely different from 1877 to 1927, and if we take the estimate given above of an equal amount absorbed by the soil from other sources, it would appear that the soil would acquire about 14 to 15 lb. sulphur per annum, apart from the amount added in the fertilizers and manures. This ignores any sulphur which may be added in the rain in forms other than sulphuric acid and sulphates. It would, therefore, mean an addition, apart from the manures, of not more than 750 lb. sulphur per acre in the 50 years of the experiment.

On the other hand, the loss of sulphur from the soil would be due either to the amount taken away by the crop itself or to that lost by drainage. The former, for a normal barley crop, was estimated by Dymond *et al.* (1905) as 6·1 lb. per acre. A more recent estimate by Lipman and Conybeare (1936) states that a 50-bushel crop of wheat removes 10·2 lb. sulphur per acre per annum. In view of the much smaller yields of barley in this experiment, we may take Dymond's figure as not far off the truth. The other main source of loss (apart from erosion) would be in drainage. We have no data from this or any similar soil as to the amount in the drainage water. There are, however, the very old determinations by Voelcker (see Hall, 1905) at Rothamsted where the mean amount of sulphur as sulphates draining from all the plots on Broadbalk Field works out at 30·6 lb. sulphur per acre per annum.

From these considerations it would seem that, apart from the manures applied, the additions would be of the order of 15 lb. per annum, and the removals of 36 lb. each year. On the other hand, the drainage at Woburn is very much freer than at Rothamsted and the loss may be in fact much greater.

Samples were taken of the soil, to 9 in. deep, of the plots noted above as follows:

1876 from the area as a whole;
1888 from all plots;
1898 from all except Plot 11b;
1913 from Plot 2 only;
1916 from Plots 1, 2, 3, and 5;
1927 from Plots 1, 2, 3, 4, 5.

The earlier samples were taken by blocks from three points on each plot and the samples so obtained were mixed. The later samples, after 1913, were taken by numerous auger holes over the plots in question.

The determinations of the various forms of sulphur were made, except as regards the total sulphur, by the methods used by Evans and Rost (1945) in their determination of sulphur in Minnesota soil. The total sulphur was determined by the method recommended by the A.O.A.C. (U.S.A.), by fusion of the soil with sodium peroxide. The figures for carbon, nitrogen, and pH value of the soils are those reported by Crowther (1936) from his examination of samples of these soils kept at Rothamsted. Non-sulphate sulphur can be obtained by subtracting the value for organic sulphur and sulphate sulphur from the total sulphur.

The actual values obtained for (*a*) sulphur as sulphate, (*b*) organic sulphur, and (*c*) humus sulphur are shown in the following table.

Plot	pH *value*	C	N	*Total* S	S *as sulphate*	*Organic* S	*Humus* S
		%	%	p.p.m.	p.p.m.	p.p.m.	p.p.m.
1876. Surface 9 in.							
	6·1	1·49	0·156	34·5	1·9	18·5	8·1
1888. Surface 9 in.							
1	5·8	1·26	0·144	22·3	4·1	16·5	9·1
2	5·4	1·34	0·143	30·3	1·6	15·1	7·6
3	6·0	1·33	0·143	45·3	2·7	17·8	9·1
4	6·0	1·19	0·122	37·1	1·8	14·4	7·2
5	5·5	1·28	0·134	63·2	2·2	17·2	10·3
11b	6·1	1·57	0·160	50·8	2·2	19·9	8·4
1898. Surface 9 in.							
1	5·4	1·19	0·135	65·9	6·3	14·4	11·3
2	4·9	1·16	0·127	42·6	3·6	15·1	8·4
3	5·9	1·15	0·120	60·4	2·2	12·3	8·6
4	5·7	1·09	0·111	33·0	2·5	15·8	7·2
5	5·0	1·03	0·112	45·3	4·7	16·5	9·1
1913. Surface 9 in.							
2	?	?	?	45·3	4·1	13·0	12·4
1916. Surface 9 in.							
1	?	1·07	0·106	39·8	2·7	13·7	8·2
2	?	?	?	49·4	4·7	14·4	13·4
3	?	?	?	42·6	1·6	15·8	12·6
5	?	?	?	37·1	4·9	13·7	11·4
1927. Surface 9 in.							
1	5·5	0·96	0·094	39·3	3·3	13·1	7·7
2	4·5	0·92	0·093	67·3	6·0	14·4	13·5
3	5·9	1·04	0·105	59·1	1·7	11·0	6·6
4	6·0	0·88	0·089	41·2	4·7	12·4	10·5
5	4·8	1·02	0·100	39·8	3·0	11·0	?

Discussion

The first conclusion from these figures is the very great constancy of the figures throughout the 50 years of the experiment. Apart from the amount of sulphur added in the manures, which is not capable of making much difference in the very small proportion of this constituent in the soil, there does not seem, on the average, to be much removal of the available sulphur by the crops of barley and the effect of drainage, whether this be in the form of sulphate or of organic sulphur. In other words, the amount of sulphur brought down in rain and that obtained from other sources has been sufficient to maintain the amount of sulphur in the soil, even when no sulphur whatever has been added, as in Plots 1

and 3. The mean amount of sulphur in its various forms at each sampling of the soils, irrespective of the manuring, has been as follows (for Plots 1 to 5):

Year	*Total* S	S *as sulphate*	*Organic* S	*Humus* S
	p.p.m.	p.p.m.	p.p.m.	p.p.m.
1876 .	34·5	1·9	18·5	8·1
1888 .	39·6	2·5	16·2	8·7
1898 .	49·4	3·9	14·8	8·9
1916* .	42·2	3·5	14·4	11·4
1927 .	49·3	3·7	12·4	9·6†

* In 1916 the figures are for Plots, 1, 2, 3, and 5 only.
† In 1927 the figure for humus sulphur is for Plots 1 to 4 only.

As regards the different plots, there seems to be a very slow but steady building up of the sulphate sulphur in Plot 2, treated every year with sulphate of ammonia, even more than in Plots 4 and 5, which really receive a very much larger amount of sulphur in the fertilizers used. This may be due to a tendency to the formation of a hard or 'pan' layer in this plot. This is doubtful, however, as the amount of sulphate sulphur has proved extremely variable and this variability may be due to the samples being taken at different times of the year when drainage was active or otherwise. Others (see Evans and Rost, 1945) have found the sulphate very variable indeed in soils and conditions not widely dissimilar.

There is a general decrease in the amount of organic sulphur during the 50 years, corresponding closely to the reduction in the amount of carbon in the soils. In other words, the sulphur content of the organic matter (the latter being represented by the carbon percentage) does not seriously change during the whole period of the experiment. The following figures show this.

Year	*Carbon A*	*Organic sulphur B*	*A/B*
	%	p.p.m.	
1876 .	1·49	18·5	80·5
1888 .	1·33	16·8	79·1
1898 .	1·21	14·8	81·8
1927 .	0·96	12·4	77·4

It is clear that as the organic matter decays, the sulphur in it is converted into other forms.

The method used for determining the humus sulphur, that is to say the sulphur contained in the organic material peptized by ammonia, is not very satisfactory, but the figures indicate that there is no decrease in the amount of this form such as occurs in that in the total organic sulphur. It forms about 22 per cent. of the total sulphur but a much larger proportion of the organic sulphur. As time has gone on, the

proportion that the humus sulphur forms of the organic sulphur increases very markedly. Taking all the treatments together, it was 44 per cent. in 1876, 54 per cent. in 1888, 60 per cent. in 1898, 79 per cent. in 1916, and 76 per cent. in 1927.

Taking together the two plots to which no sulphur has been added in the manures (Plots 1 and 3), the organic sulphur remaining after 50 years was 65 per cent. of that at the commencement, and in the plots which have had dressings containing sulphur, the sulphur remaining was 68 per cent. of the original. It is evident that the addition of the manures has little to do with the falling off in the organic sulphur.

One more point remains. It is clear that the main source of loss of sulphur from the soil is in the drainage water. In a free-draining soil like the present, is there any evidence of its accumulation in the subsoil? Samples were available of the subsoil between 18 and 27 in. deep in 1876, and between 9 and 18 and between 18 and 27 in. deep in 1888. These were examined for the content of sulphur in various forms with results which are shown in the following table.

Plots	*Total* S	S *as sulphate*	*Organic* S
	p.p.m.	p.p.m.	p.p.m.
1876. Soil 18–27 in. deep			
	15·1	1·4	6·2
1888. Soil 9–18 in. deep			
1 . .	15·1	2·5	10·3
2 . .	34·3	1·6	7·6
3 . .	33·0	1·1	7·6
4 . .	43·9	1·2	5·5
5 . .	53·6	2·2	6·9
11b. .	39·8	3·0	10·3
1888. Soil 18–27 in. deep			
1 . .	27·5	1·9	9·6
2 . .	23·3	2·2	8·2
3 . .	34·3	0·8	4·8
4 . .	31·6	1·5	2·7
5 . .	31·6	1·4	4·8
11b. .	31·6	1·6	6·9

Taking all the plots together, it is clear that, 11 years after the experiment was started, the mean amount of total sulphur and of sulphate sulphur was slightly less in the lower depths than in the surface layers, while the organic sulphur was very much reduced. This is perhaps what would be expected if there was no accumulation of sulphur in the lower layers of the soil. In the individual plots the same conclusion would seem to apply, and it seems clear that such sulphur as drains away, probably in the form of sulphates, passes during the winter (when most of these samples were taken) into the lower layers of the soil which are out of the range of barley roots.

Summary

A study of the content of sulphur in various forms in a soil which has borne spring barley each year for 50 years under various manures makes it clear that under normal rural conditions the sulphur received by the soil from rain and other atmospheric sources is amply sufficient to maintain the sulphur content of the soil. This applies whether the soil is unmanured or has an application of ammonium salts, nitrate of soda, or these materials with a dose of phosphates, potash, and other mineral manures. During the 50 years when the application of these materials was made every year, without any organic manures, the carbon content of the soil was reduced and the amounts of total and of organic sulphur were reduced almost to the same extent, but the humus sulphur remained very much steadier.

In a free-draining soil such as that under study there is no evidence of a tendency of the sulphur to be carried down and remain in the subsoil within the range of barley roots.

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RESIDUAL EFFECTS OF PHOSPHATE FERTILIZERS ON A WEALDEN SOIL

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Introduction

EXPERIMENTS carried out during the war years to test alternative phosphate fertilizers have been described (Crowther and Cooke, 1951). Most were annual experiments and it was rarely possible to measure second-year effects. One experiment (Centre 43/25) was on land farmed by the Haywards Heath Central School in Sussex. The soil was a fine sandy silt loam (of pH 5·6) overlying Wealden Beds. The site was badly drained, red-brown mottling occurred in the subsoil down to the maximum depth examined. The experiment laid down in 1943 tested Silico-phosphate and Bessemer basic slag against superphosphate. Swedes grown in 1943 responded well to phosphate. Potatoes were planted in 1944, dressings of N and K fertilizers being given to all plots, but no more phosphate was applied; the crop was very poor and there were only small increases in yield from heavy dressings of superphosphate applied the year before. The School authorities allowed the site to be used for several years, and in 1945 the experiment was redesigned to provide information on the residual value of superphosphate. A complete phosphate balance sheet was prepared for each treatment for the period 1945–50. At the end of the period soil samples from each plot were examined (by J.K.R.G.).

Experimental

Design of the field experiment

The experiment laid down in 1943 was a 5×5 Latin Square having individual plots 5 yds. long and 4 yds. wide ($\frac{1}{240}$ acre) separated by grass paths. The 1945 modification of the experiment tested:

1. No phosphate
2. Superphosphate at 0·2 cwt. P_2O_5 per acre applied for each crop
3. Superphosphate at 0·5 cwt. P_2O_5 per acre
4. Superphosphate at 1·0 cwt. P_2O_5 per acre
5. Poultry manure supplying 1·0 cwt. P_2O_5 per acre

(3, 4, 5: applied in alternate years)

These treatments were arranged in five blocks of randomized plots in such a way that each of the 1945 treatments fell once only on each of the 1943 treatments.

The two heavier dressings of superphosphate and the dressing of poultry manure were applied in 1945, 1947, and 1949. The light dressing (0·2 cwt. P_2O_5 per acre) of superphosphate applied for each crop was intended as a standard for measuring the residual effects of heavier dressings of superphosphate (and poultry manure). After the 1945 crop

of beetroot was lifted, superphosphate supplying 0·2 cwt. P_2O_5 per acre was applied to appropriate plots for a crop of carrots that failed.

All phosphate dressings were applied in terms of *total* P_2O_5. The poultry manure used was a commercial preparation containing 3·3 per cent. P_2O_5. (Poultry manure contains a considerable proportion of organic phosphate (Ghani, 1941), and such compounds may not be precipitated by soil constituents as rapidly as the water-soluble phosphate in superphosphate.)

Adequate quantities of nitrogen and potassium fertilizers were applied uniformly to all plots of the experiment for each crop. No allowance was made for the extra nitrogen introduced by poultry manure.

Results of the field experiment

Yields obtained in each year are stated in Table 1 together with the amounts of phosphate removed by the crops harvested.

TABLE 1

Yields of Crops in the Field Experiment at Haywards Heath

	No phosphate	*Superphosphate*			*Poultry manure*	*Standard error*
cwt. P_2O_5 per acre applied .	0·0	0·2 (to each crop)	0·5	1·0	1·0	..
			(to alternate crops)			
	Yields in tons per acre					
First-year crops						
1945 Beetroot						
Roots	0·09	0·45	1·51	2·23	2·80	0·31
Tops	0·47	1·02	1·77	1·71	2·58	0·38
1947 Swedes						
Total produce . . .	0·84	2·98	7·16	12·00	12·47	0·62
1949 Swedes						
Total produce . . .	0·98	2·58	3·11	5·66	4·86	0·25
Second-year crops						
1946 potatoes	10·63	12·49	11·47	13·57	12·49	0·62
1948 potatoes	6·59	9·07	7·74	8·79	10·24	0·25
1950 potatoes	7·35	7·63	8·17	6·05	7·32	0·83
	Total amounts of P_2O_5 in crops harvested (cwt. per acre)					
First-year crops						
1945 Beetroot . . .	0·001	0·005	0·018	0·030	0·031	..
1947 Swedes . . .	0·005	0·020	0·047	0·099	0·117	..
1949 Swedes . . .	0·009	0·036	0·049	0·089	0·070	..
Second-year crops						
1946 potatoes	0·111	0·140	0·143	0·169	0·150	..
1948 potatoes	0·079	0·118	0·104	0·116	0·152	..
1950 potatoes	0·091	0·097	0·111	0·085	0·100	..

All the first-year crops responded significantly ($P = 0.05$) to phosphate, and there were no significant differences between poultry manure and superphosphate supplying equal quantities of P_2O_5. Potatoes grown in 1946 and 1948 responded significantly to superphosphate applied in previous years; in 1948 poultry manure gave a significantly higher yield of potatoes than superphosphate supplying the same amount of P_2O_5 (dressings were applied in 1945 and 1947). Phosphate had no significant effects on the yields of potatoes in 1950.

The amounts of dry matter produced and the total amounts of phosphate removed by the crops are stated in Table 2, summing all first-year crops and all second-year crops separately. Poultry manure produced slightly more dry matter in first-year crops than superphosphate supplying the same total amount of P_2O_5, the amounts of phosphate removed from these two sources were identical. 0·2 cwt. P_2O_5 per acre applied each year as superphosphate produced somewhat more dry matter from the three second-year crops than 1·0 cwt. P_2O_5 per acre applied to the first-year crops. The total amount of P_2O_5 recovered from these small annual dressings by potatoes was similar to the amount recovered from 0·5 cwt. P_2O_5 per acre (as superphosphate) applied to the first-year crops.

TABLE 2

Total Amounts of Dry Matter produced and of Phosphate taken up by three First-year Crops, three Second-year Crops, and by all six Crops

	No phosphate	*Superphosphate*			*Poultry manure*
P_2O_5 dressings, cwt. per acre	0·0	0·2 (each year)	0·5	1·0	1·0
			(to alternate crops)		
		Sums of three first-year crops			
cwt. per acre					
Dry matter	4·4	12·8	25·8	40·5	44·4
P_2O_5 in crops	0·015	0·061	0·114	0·218	0·218
		Sums of three second-year crops			
cwt. per acre					
Dry matter	102·2	121·1	109·5	117·1	121·7
P_2O_5 in crops	0·281	0·355	0·358	0·370	0·402
		Sums of all six crops			
cwt. per acre					
Total P_2O_5 added as fertilizer	0·0	1·4	1·5	3·0	3·0
Dry matter produced	106·6	133·9	135·3	157·6	166·1
P_2O_5 in crops	0·296	0·416	0·472	0·588	0·620

The total production of dry matter and total uptake of P_2O_5 for all six crops are also summarized in Table 2. The dry matter produced by 0·2 cwt. P_2O_5 per acre applied to each crop was about equal to the amount which would have been given by a similar total amount of P_2O_5 applied to the first-year crops only. The six crops recovered rather less P_2O_5 from

these small annual dressings than would have been obtained from the same total amount of P_2O_5 given to the first-year crops. Poultry manure gave higher total yields and phosphate recoveries than superphosphate applied at equivalent rate and was therefore a more efficient phosphate fertilizer than superphosphate on this particular field.

The percentages of the added phosphate which had been recovered by the crops grown over the 6 years were calculated. They were:

from		*Total per cent.* P_2O_5 *recovered*
Superphosphate at 0·2 cwt. P_2O_5 per acre for each crop		9
Superphosphate at 0·5 cwt. P_2O_5 per acre	for alternate crops	12
Superphosphate at 1·0 cwt. P_2O_5 per acre		10
Poultry manure supplying 1·0 cwt. P_2O_5 per acre		11

These are, of course, only apparent recoveries. Fertilizer phosphate, by promoting more extensive root growth, may enable crops to take up larger quantities of soil phosphate than are removed by crops grown on unmanured plots. It is not possible to determine the proportions of phosphate in crops which are derived from soil and from fertilizer unless 'tagged' phosphates are used.

Examination of soil samples

Approximately 90 per cent. of the phosphate added (amounting on heavily manured plots to 2·7 cwt. P_2O_5 per acre) was not removed by the crops. Assuming a conventional weight for the cultivated layer of soil (2,000,000 lb. per acre) this amount is equivalent to 15 mg. P_2O_5 per 100 g. soil. Such quantities are easily detected by methods of acid extraction used to determine easily soluble phosphate. Soil samples taken from all plots after the 1950 harvest were analysed.

Dilute acid-soluble phosphate was determined by three methods:

1. 6·25 g. soil were leached with 250 ml. 0·5 N acetic acid.
2. 2 g. soil were shaken with 200 ml. 0·5 N acetic acid for 2 hours.
3. 3 g. soil were shaken with 7 ml. 0·3 N HCl for 2 minutes.

Phosphate was determined in the extracts by the method of Truog and Meyer (1929).

Total phosphate was determined by digesting with nitric, hydrochloric, and perchloric acids (Burriel and Hernando, 1949), P_2O_5 being determined by the method of Barton (1948). The results of the soil analyses are summarized in Table 3, averaging the data obtained from the soil of each similarly treated plot.

Discussion

The experimental treatments had not increased the total amount of phosphate present in the cultivated layer of soil (0–6 in.) and no appreciable proportion of the dressings applied over the 6 years remained soluble in dilute acids. Increases in crop yields produced by superphosphate applied a year previously were equal only to those given by

TABLE 3

P_2O_5 determined in Soil Samples taken in Autumn 1950
(mg. P_2O_5 per 100 g. soil)

Treatment	P_2O_5 applied cwt./acre	Total P_2O_5	Easily soluble P_2O_5, extracted by		
			0·5 N acetic acid (leaching)	0·5 N acetic acid (shaking)	0·3 N HCl
1 No phosphate	0·0	97	0·6	1·8	0·9
2 Superphosphate	0·2 (annual)	97	0·7	1·9	1·0
3 Superphosphate	0·5 (biennial)	96	0·7	2·0	1·0
4 Superphosphate	1·0 (biennial)	97	0·9	2·2	1·1
5 Poultry manure	1·0 (biennial)	97	0·6	1·6	1·1
Standard error	..	2·7	0·11	0·28	0·18

about one-fifth as much superphosphate freshly applied. Crop yields did not suggest that soil-phosphate reserves were being built up, and the whole of the evidence points to a rapid 'decay' of phosphate in this soil.

Water-soluble phosphate may combine with iron and aluminium and form compounds which are insoluble in dilute acids and useless to crops. If such reactions had occurred in the soil of dressed plots in this experiment the total amount of phosphate would have increased. Since there were large differences between the amounts of phosphate applied as fertilizer and the amounts recovered by the crops the greater part of the applied phosphate must have moved down the soil profile below the cultivated layer. McGregor (1953) showed that phosphorus moved down the soil profile in an uncultivated pasture in Scotland, such movement being most marked in poorly drained soils. Neller *et al.* (1951) showed that 80 per cent. of the phosphate applied as superphosphate was leached out of the surface layer of very acid sandy soils in Florida during the course of a season.

It is very difficult to determine the residual value of phosphate fertilizers where land and facilities are limited. The greatest difficulty at Haywards Heath was to establish satisfactory crops on soil having very poor structure. The fine sandy silt loam had very little natural crumb structure and was not improved by winter frosts. It capped badly in heavy rain. With the rotation followed, no bulky crop residues were returned to the soil, and the root systems of the crops grown did not improve soil aggregation. Any organic material which might have been added to improve soil structure (straw, compost, peat) would have added phosphate.

Summary

A field experiment was continued for 6 years, using a 2-year rotation of beetroot or swedes followed by potatoes. Normal dressings of superphosphate and also poultry manure were applied to the first-year crops.

On other plots a small dressing of superphosphate (supplying 0·2 cwt. P_2O_5 per acre) was applied to each crop.

For second-year crops of potatoes a fresh dressing of superphosphate supplying 0·2 cwt. P_2O_5 per acre gave yields roughly equal to those given by 1·0 cwt. P_2O_5 per acre applied as superphosphate the year before.

Poultry manure used to supply phosphate had slightly greater effects on both first and second-year crops than superphosphate supplying the same amount of P_2O_5. Higher yields from poultry manure than from superphosphate may have been due in part, to extra nitrogen supplied by the poultry manure, for which no allowance was made.

Only 10 per cent. of the phosphate applied had been removed by the crops grown. Soil samples from individual plots were examined when the experiment was concluded. Total soil phosphate and dilute-acid-soluble soil phosphate had not been increased by experimental dressings of phosphate fertilizer. It is suggested that much of the fertilizer phosphate applied had moved down the soil profile below the cultivated layer.

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OBSERVATIONS ON THE DETERMINATION OF TOTAL ORGANIC PHOSPHORUS IN SOILS

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Up to half or more of the total P in soils may be present in organic forms [1, 15]. Considerable importance, therefore, attaches to methods for determining the total organic P.

A comprehensive review of organic P and its estimation in soils has recently been given by Black and Goring [1]. Two main types of method can be used. In one, the organic P is measured as the increase in inorganic P extracted by a suitable acid solution after the soil organic matter has been destroyed by ignition or by treatment with an oxidizing agent such as H_2O_2. The other main type depends on alkaline extraction of the organic P after acid pretreatment of the soil to remove bases. The organic P is then estimated by difference between the total and inorganic P in the extracts; both these estimations are done colorimetrically, the inorganic P being determined directly in the extracts and the total P after treatment to destroy the organic matter. Thus, although the two types of method represent a different approach, they both involve oxidation of organic matter; in the first case this is done by treating the soil before extraction whereas in the second it is done in the extracts.

Apart from the disadvantage that the values are obtained by difference, organic P estimations are subject to many uncertainties [1]. The main requirements in ignition–acid extraction methods are to ensure complete release and recovery of the organic P and avoid changes in the solubility of the inorganic P during the ignition. In alkaline extraction procedures, the main problem is to arrive at a combination of acid pretreatment and alkaline extracting agent which ensures complete extraction of the organic P without bringing about hydrolysis. In view of these conflicting requirements, it is not surprising that a wide variety of procedures has been used and that different workers have obtained contradictory results [1].

The present results were obtained during a study of the distribution of phosphorus in a series of soil profiles from long-term field experiment areas. The total organic P was determined in the first place by a slight modification of the very simple and rapid Ignition–0·2 N H_2SO_4 extraction method used by Mattson, Williams, and Barkoff [10]. To check the results, the organic P content of the topsoils was determined by the hot ammonia extraction method of Pearson [11]. The results showed large discrepancies between the two methods which made it necessary to test the validity of the estimations. To this end, the effects of varying the experimental conditions in the two methods have been

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investigated and parallel tests carried out using sodium hydroxide as the extracting agent.

Experimental

The soils used represent various horizons from seven contrasting profiles. They cover the four main soil associations in north-east Scotland [6, 7, 9], and include three pairs of corresponding well-drained and poorly drained profiles as indicated in Table 5.

The essential details of the main analytical procedures are summarized below. Details of subsidiary tests are given later in conjunction with the results.

Ignition–0·2 N H_2SO_4 *extraction method.* 2 g. air-dry soil <2 mm. was ignited in a silica crucible for 1 hour at 550° C. The ignited residue and a fresh 2 g. lot of unignited soil were then extracted overnight (16½ hours) with 100 ml. of 0·2 N H_2SO_4 on an end-over-end shaker. Inorganic P was then determined by direct colorimetric estimation on the extracts, using the $SnCl_2$ method summarized below. The difference, Inorganic P from the Ignited Soil—Inorganic P from the Unignited Soil, was taken as the Total Organic P in the soil.

Hot 0·5 N *ammonia extraction method.* 1 g. air-dry soil<100 mesh was added to about 20 ml. 0·1 N HCl in a beaker, stirred occasionally for about 10 min., transferred to a funnel and then leached with 0·1 N HCl to give a total leachate of 100 ml.

The filter-paper with the residue was transferred to a 500-ml. conical flask and disintegrated by vigorous shaking with a little 0·5 N ammonia. The volume was then made up to 400 ml. with 0·5 N ammonia and the flask fitted with a rubber stopper with Bunsen valves and placed in an oven at 90° C. for 16 hours. After cooling, 5 g. ammonium sulphate was added to assist flocculation and the contents made up to the original volume with ammonia and filtered.

Proportionate volumes of the acid and alkaline extract were then mixed and suitable aliquots of the mixed extract taken for analyses. For inorganic P, the bulk of the organic matter (α humus) was removed by acidifying to about pH 3, warming, filtering, and washing with hot water. For total P, the aliquot was evaporated to dryness with 1 ml. 10 per cent. magnesium nitrate solution, ignited, digested for an hour with 0·5 N HCl, filtered, washed, and adjusted to pH 3 using p-nitrophenol as indicator. The difference, Total—Inorganic P, gives the Organic P in the extracts.

Cold 0·1 N NaOH *extraction method.* 0·5 g. air-dry soil <100 mesh was digested on a water-bath for 1 hour with 25 ml. 0·1 N HCl, transferred to a funnel and leached with further portions of hot acid to give a volume of 100 ml.

The filter-paper with soil was transferred to a 250 ml. centrifuge tube, disintegrated by vigorous shaking with 200 ml. 0·1 N NaOH, and extracted for 16½ hours on an end-over-end shaker. After adding 1 g. NaCl to assist flocculation the tube was centrifuged and as much as possible of the clear extract decanted. A volume of fresh 0·1 N NaOH equal to the volume of extract taken off was then added to the tube and

the extraction repeated. In this way the NaOH extract could be repeated as often as desired, and since the volume of extract decanted each time was noted the small carry-over of P from one extract to the next was easily corrected for.

The total and inorganic P were determined as already indicated, using either the mixed extracts or the separate extracts, depending on the information required.

Colorimetric estimations. All determinations were carried out using a Spekker Absorptiometer as described by Williams and Stewart [14], the reagents being 4 ml. 2·5 per cent. ammonium molybdate in 10 N H_2SO_4 and 0·8 ml. freshly prepared 1 per cent. solution of $SnCl_2.2H_2O$ in 10 per cent. by vol. HCl, made up to a final volume of 100 ml. and allowing 30 min. for colour development. The results throughout were evaluated from calibration curves prepared under strictly comparable conditions.

The validity of the colorimetric estimations on the various extracts has been confirmed. Within the range of the method, the inorganic P estimations are independent on the amount of extract taken and give complete recoveries of added phosphate. For total P, the colorimetric estimations show very satisfactory agreement with the Lorenz gravimetric method [12].

Results and Discussion

Tests on the ammonia method (Table 1)

The results in Table 1 show that the Ignition values are from two to four times greater than the values by the simplest form of the Pearson method [11]. The differences are many times larger than normal variations between replicates. Since the main sources of error in alkaline extraction methods are incomplete extraction and hydrolysis of the organic P, the most likely explanation is that the Pearson values are too low. These possibilities were examined by the following tests.

Effect of ammonia concentration and repeated extraction. Even with tightly fitting Bunsen valves there was a major loss of ammonia during the digestion, the final concentration being 0·3–0·4 N. A comparison between 1·0, 0·5, and 0·2 N ammonia was, therefore, carried out on soil 3 A, using the ordinary pretreatment of 1 g. soil with 100 ml. cold 0·1 N HCl. The organic P values were 64, 53, and 51 mg. P_2O_5 per 100 g. soil, respectively. The 1·0 N solution extracts appreciably more organic P than the other two, but the value is still very small compared with the value of 188 mg. by the Ignition method. No appreciable amount of organic P was obtained when the extractions were repeated on the residues. In agreement with the results of Pearson [11], it appears that no major increase in the organic P values can be obtained by increasing the ammonia concentration or using successive extractions.

Effect of acid pretreatment (Table 1). The extraction of organic P by alkaline solutions is known to depend on the acid pretreatment [1]. Two modifications of the normal treatment of 1 g. soil with 100 ml. 0·1 N HCl were therefore tested. These were treatment with 200 ml. cold

acid and treatment with 200 ml. hot acid, including a preliminary digestion with 50 ml. for 1 hour on the water-bath. The differently treated samples were then extracted by the standard Pearson procedure. The results in Table 1 show that doubling the amount of cold acid markedly increased the organic P value. Hot acid produced a further considerable increase for soil 3 A and a slight increase for 1 A, but the other soils show no significant effect of heating. The pretreatment with 100 ml. cold 0·1 N HCl is, therefore, inadequate, and this partly accounts for the low values by the ordinary Pearson method. But it is not the only factor. Even after the hot acid treatment the values are still much lower than by the Ignition method, and it is clear that no appreciable improvement can be expected from increasing the severity of the pretreatment further.

Effect of temperature on extraction and hydrolysis. 0·5 g. lots of soil <100 mesh from samples 1 A and 5 A were treated with 100 ml. cold 0·1 N HCl and then extracted for 16 hours with 200 ml. 0·5 N ammonia at room temperature. The total organic P extracted was 61 and 69 mg. P_2O_5 per 100 g. soil, respectively, compared with 78 and 88 for the corresponding extraction at 90° C., Table 1. In agreement with the

TABLE 1

Organic Phosphorus Values by the Ignition Method and by Hot-Ammonia Extraction following Different Acid Pretreatments—mg. organic P_2O_5 *per 100 g. O.D. soil*

Sample no.	*Ignition method*	**Hot 0·5 N ammonia extraction after pretreatment of 1 g. soil with:*		
		100 ml. cold 0·1 N HCl	*200 ml. cold 0·1 N HCl*	*200 ml. hot 0·1 N HCl*
1 A	124	63	78	84
2 A	84	31	49	49
3 A	188	53	100	128
4 A	96	20	61	60
5 A	150	66	88	90
6 A	105	43	71	..
7 A	232	90	..	138

* Total organic P_2O_5 in $HCl+NH_4OH$ extracts.

results of Pearson [11], the extraction at room temperature is considerably less effective. But the possibility still remains that the efficiency of the hot extraction is reduced by hydrolysis. To test this point, inorganic P was determined in aliquots of the cold ammonia extracts and in aliquots of the same extracts after digesting on a water-bath for 16 hours, the volume being maintained by frequent additions of 0·5 N ammonia. In both cases the inorganic P content increased by 20–25 per cent. after heating. There is little doubt therefore that some hydrolysis occurs during the standard extraction at 90° C.

The above tests are not exhaustive but they suffice to show that the values by the ordinary Pearson method are too low and that the main causes are incomplete extraction and hydrolysis of the organic P. The

acid pretreatment is important, but apart from this, it is clear that on the present soils at least, ammonia has very definite limitations as an extractant of organic P. It was decided therefore to try sodium hydroxide which has been found to be effective by several workers [2, 13, 16].

Tests with 0·1 N NaOH (*Tables 2, 3, and 4*)

The alkaline extraction procedure has already been described. The soil/NaOH ratio of 1/400 was adopted for comparison with the Pearson ammonia extraction.

Effect of acid pretreatment (*Table 2*). In view of the marked effects found with the Pearson method, four acid pretreatments were compared using a single extraction with cold 0·1 N NaOH. The first two of these were the cold and hot 0·1 N HCl treatments, already mentioned, in which 0·5 g. soil <100 mesh was treated with a total of 100 ml. acid. The third consisted of allowing 0·5 g. soil <100 mesh to stand overnight with 25 ml. 4 N HCl., after occasional stirring, then transferring to a funnel and leaching to 100 ml. with 0·01 N HCl. This treatment was adapted from Wrenshall and Dyer [16] to fit in with the present scheme. In the fourth pretreatment, similarly modified from C. H. Williams [13], 0·5 g. soil <100 mesh was shaken with 50 ml. of 1 per cent. 8-hydroxyquinoline in 2·5 per cent., by vol., acetic acid for 16 hours at room temperature; transferred to a funnel and leached to a total filtrate of 100 ml. with 2·5 per cent. acetic acid. Total and inorganic P was determined to give the organic P in the individual acid and alkaline extracts, except for the hydroxyquinoline extract where the interfering effect of the organic reagent hinders the direct determination of inorganic P.

Many of the variations according to pretreatment in Table 2 are small

TABLE 2

Comparisons of Acid Pretreatments using Single Extraction with Cold 0·1 N NaOH—*mg. organic* P_2O_5 *per 100 g. O.D. soil*

Sample no.	*Cold* 0·1 N HCl			*Hot* 0·1 N HCl			*Cold* 4 N HCl			8(OH)-*Quin-Acetic*
	Acid ext.	NaOH *ext.*	*Total*	*Acid ext.*	NaOH *ext.*	*Total*	*Acid ext.*	NaOH *ext.*	*Total*	NaOH *ext.*
1 A . .	2	102	104	6	104	110	58	47	105	106
2 A . .	3	63	66	14	66	80	28	37	65	64
3 A . .	4	153	157	7	166	173	69	97	166	162
4 A . .	6	63	69	15	71	86	..	..	..	80
5 A . .	6	97	103	8	114	122	48	47	95	119
6 A . .	4	75	79	13	76	89	36	47	83	81
Means excluding 4 A .	4	98	102	10	105	115	48	55	103	106

and unimportant. But comparison of the three HCl treatments on the basis of total organic P in the acid and NaOH extracts shows that the hot 0·1 N HCl treatment gives the highest values and is therefore

the best. The results after the prolonged treatment with 4 N HCl are of particular interest. It is no better than the much shorter and less drastic treatment with cold 0·1 N acid, and gives a markedly different distribution of P between the acid leachate and the NaOH extract. Unlike the 0·1 N HCl extracts, the 4 N extracts contain quite large amounts of organic P with the result that the subsequent NaOH extracts contain correspondingly less. The detailed figures are not included, but they show that the 4 N acid also extracts much larger amounts of inorganic P, with the result that there are only small amounts in the subsequent NaOH extracts. These contrasts illustrate the point that the cold 4 N treatment is considerably more drastic than the hot 0·1 N HCl treatment. The somewhat lower organic P values after the 4 N treatment cannot therefore be due to lower efficiency of the NaOH extraction. It seems probable that the prolonged treatment with 4 N acid hydrolyzes some of the organic P.

The organic P values after the acetic-hydroxyquinoline treatment refer to the NaOH extracts only. Even so, they compare favourably with the totals after the cold 0·1 N and cold 4 N HCl treatments, and are not much lower than the totals from the hot HCl procedure. It is possible that because of complex formation with Fe and Al the acetic-hydroxyquinoline extracts may contain appreciable amounts of organic P which if included would make this pretreatment superior to all the others. But since, as already explained, it is difficult to estimate it, there is no gain in practice. From the practical point of view, the relatively simple and rapid hot 0·1 N HCl pretreatment is the best, and the general trend of the results suggests that it is about the optimum for the present soils.

Effect of temperature and repeated extraction (*Tables 3 and 4*). The effect of digesting with 0·1 N NaOH for 16 hours at 90° C., as in the Pearson method, was tested, using the hot 0·1 N HCl pretreatment. The results are given in Table 3. Samples 1 A, 2 A, and 4 A show no

TABLE 3

Effect of Heating and Repeated Extraction on Organic Phosphorus Values by the 0·1 N NaOH *Method—mg. organic* P_2O_5 *per 100 g. O.D. soil*

Sample no.	*Hot* HCl *ext.* + *one hot* NaOH *ext.*	*Hot* HCl *ext.* + *one cold* NaOH *ext.*	*2nd cold* NaOH *ext.*	*Total from* HCl + *two cold* NaOH *exts.*
1 A	105	110	4	114
2 A	83	80	3	83
3 A	154	173	5	178
4 A	86	86	4	90
5 A	112	122	10	132
6 A	78	89	9	98
Means	103	110	6	116

clear effect of heating, but for the remainder the hot extraction gives appreciably lower values. The effect of 16 hours digestion on the water-

bath on the inorganic P contents of the cold NaOH extracts was also determined. The results, Table 4, show clear increases ranging from 8 to 22 mg. P_2O_5 per 100 g. soil. It appears, therefore, that any increase

TABLE 4

Effect of Hot Digestion on Inorganic Phosphorus Content of Cold 0·1 N NaOH Extracts—mg. inorganic P_2O_5 per 100 g. O.D. soil

Sample no.	*Cold ext.*	*Heated ext.*	*Increase*
1 A	38	60	22
2 A	36	44	8
3 A	102	117	15
4 A	97	108	11
5 A	29	42	13
6 A	29	41	12
7 A	100	117	17

in the extracting power of 0·1 N NaOH by raising the temperature to 90° C. is counteracted by hydrolysis of the organic P, and that the cold extraction is preferable. The effect of intermediate temperatures has not been examined. It is possible that some degree of heating might give higher organic P values than are obtained at room temperature, but in view of the occurrence of hydrolysis it is unlikely that any major increase can be obtained.

The cold NaOH extraction was repeated twice on the residues. The values in the fourth column of Table 3 show that the organic P contents of the second extracts are very small. The third extracts contained no significant amount.

Comparison of hot 0·5 N *ammonia with cold* 0·1 N NaOH (*Tables 1 and 2*)

Comparison of the results in Tables 1 and 2 shows that irrespective of whether the soil was pretreated with hot or cold 0·1 N HCl, the organic P value from single extractions with cold NaOH are markedly higher than the hot-ammonia values. Since the acid extracts contain only very small amounts of organic P, it is clear that cold NaOH is superior and the conclusion that the hot-ammonia values are too low is confirmed.

Comparison of the ignition and NaOH methods (*Table 5*)

The double extraction with cold 0·1 N NaOH following pre-treatment with hot 0·1 N HCl was applied to twenty-three samples covering the seven profiles. The results, together with corresponding values by the ignition method, are given in Table 5. The values by both methods are the means of at least two determinations.

In comparing the results it must be taken into account that both sets of estimations are obtained by difference. As a result, normal variations and errors in the sampling, extractions, and colorimetric estimations give rise to considerable absolute differences in the organic P values. When, as is the case for many of the subsoils, the organic P value is obtained by difference between two much larger figures it is subject to large percentage errors. For example, if the two figures concerned are

TABLE 5

General Comparison of Organic Phosphorus Values by the Ignition–0·2 N H_2SO_4 Extraction Method and by the Hot 0·1 N HCl–Double Cold 0·1 N NaOH Extraction Method—mg. P_2O_5 per 100 g. O.D. soil.

		Ignition method			*Hot* HCl + *cold* NaOH *extraction*		
		Inorganic P_2O_5 *extracted*			P_2O_5 *in* HCl + NaOH *extracts*		
Sample no.	*Depth (in.)*	*Ignited soil*	*Unignited soil*	*Org.* P_2O_5 *by diff.*	*Total*	*Inorg.*	*Org.* P_2O_5 *by diff.*
		Freely-Drained Profile on Old Red Sandstone Till					
1 A	0–6	220	96	124	240	126	114
1 B	10–14	165	52	113	178	70	108
1 C	17–21	184	65	119	196	81	115
		Poorly-Drained Profile on Old Red Sandstone Till					
2 A	0–6	184	100	84	210	127	83
2 B	9–13	136	45	91	149	68	81
2 C	15–19	99	30	69	111	51	60
		Freely-Drained Profile on Basic Igneous Till					
3 A	0–6	322	134	188	376	198	178
3 B	15–17	179	110	69	179	128	51
3 C	18–21	110	73	37	111	91	20
3 D	26–30	67	44	23	77	77	0
		Poorly-Drained Profile on Basic Igneous Till					
4 A	0–6	330	234	96	354	264	90
4 B	10–14	216	197	19	190	171	19
4 C	18–22	196	188	8	179	171	8
4 D	26–30	130	125	5	141	141	0
		Freely-Drained Profile on Granitic Till					
5 A	0–8	229	79	150	238	106	132
5 B	10–14	149	60	89	159	83	76
5 C	14–20	174	167	7	158	153	5
		Poorly-Drained Profile on Granitic Till					
6 A	0–8	191	86	105	211	113	98
6 B	11–16	94	84	10	90	77	13
6 C	22–27	120	113	7	121	121	0
		Freely-Drained Profile on Slate Till					
7 A	0–8	376	144	232	392	221	171
7 B	12–18	170	65	105	161	98	63
7 C	24–30	95	47	48	85	73	12

150 and 100, an error of +4 per cent. in the former and −4 per cent. in the latter results in a difference of 60 instead of 50, i.e. an increase of 20 per cent. In the type of determination from which the basic figures in both methods are obtained variations of ±4 per cent. represent very satisfactory reproducibility and considerably greater differences frequently occur. In the absence of extensive replication of the individual estimations and statistical treatment of the results, the great majority of the differences between the two sets of values of organic P_2O_5 in Table 5 must be regarded as being of very doubtful significance. Considering the numerous factors involved, the values on the whole are very similar and the agreement in the majority of cases is very satisfactory. The general tendency is for the Ignition values to be somewhat higher and the differences for samples 7 A, 7 B, and 7 C, representing the well-drained profile developed on slates, are considerable. The estimations on these samples have been checked, and in each case the lowest value by the ignition method is clearly higher than the highest value by the NaOH method. The markedly poorer agreement in this profile is presumably a function of the parent material and drainage conditions. In the light of this, it seems possible that the somewhat poorer agreement for the subsoils 3 C, 3 D, and 3 E of the well-drained basic igneous profile represents a real trend and is also related to the parent material and drainage. It is known [6, 7] that there are marked contrasts in the phosphate relationships of corresponding well-drained and poorly drained soils derived from slates and basic igneous till. In keeping with this, samples 4 A–4 D from the poorly drained basic igneous profile show very satisfactory agreement.

Tests on the ignition method (*Tables 6 and 7*)

The two main sources of error in the Ignition method are incomplete recovery of the released organic P and changes in the solubility of the native inorganic P during the ignition. The former would result in the organic P values being too low and cannot therefore account for the above differences between the two methods. Changes in the solubility of the inorganic P present a more complicated and less predictable problem. Depending on whether the solubility increases or decreases during the ignition, the resulting organic P value may be too high or too low. Fraps [4], Doughty [3], and Ghani [5], using precipitated phosphates and natural mineral phosphates of Fe and Al, found that ignition did affect their acid solubility. Doughty, however, found that the solubility of apatite was not affected by ignition at 800° C. But usually it is by no means certain that the various phosphates which have been tested occur in soils or are present in sufficient amounts to cause appreciable errors. The behaviour of a given phosphate in soils may also be governed by factors such as particle size and association with other soil constituents. Changes in phosphate solubility can arise indirectly as a result of changes in the activity of constituents, such as sesquioxide complexes, governing the extraction [15]. A more direct approach would be to carry out tests on the actual soils. A number of tests, such as examination of the effect of ignition on soil residues after removal of organic P by extraction or

oxidation, can be envisaged. But the additional treatments of the soil which are entailed again make the results inconclusive. Some indication of the validity of the method can, however, be obtained from consideration of the effects of varying the experimental conditions.

Effects of conditions of extraction (*Table 6*). Previous tests on other soils indicated that the organic P value was not appreciably altered by extracting for 16½ hours instead of 2 hours. Since the overnight extraction is more convenient in practice it was adopted for routine use. This finding is confirmed by the results of additional tests covering some of the present samples. From Table 6 it will be seen that the variations

TABLE 6

Effect of Period of Extraction and Acid Concentration on Organic Phosphorus Values by the Ignition Method—mg. organic P_2O_5 *per 100 g. O.D. soil.*

Sample no.	Acid normality and period of extraction							
	4 N		2 N		0·2 N		0·1 N	
	2 hrs.	*16½ hrs.*	*2 hrs.*	*16½ hrs.*	*2 hrs.*	*16½ hrs.*	*2 hrs.*	*16½ hrs.*
4 A	111	107	100	98	112	96	100	102
A 31502*	161	170	182	178	155	158	145	159
A 31496*	225	224	223	233	226	230	240	227
7 B	104	102	100	102	96	105	88	93
Means	150	151	151	153	147	147	143	145

* Samples A 31502, A 31496, and A 31492 in Tables 6 and 7 are closely comparable with samples 5 A, 7 A, and 1 A, respectively.

according to acid concentration and period of extraction are generally small and rather inconsistent. The mean values for the four soils suggest that slightly higher results may be expected when the acid concentration is increased to 2 N. The difference is very small and unimportant, but the tendency is supported by the results of another series of tests in which the four concentrations of acid were compared on fifteen of the samples using 16½ hours extraction. The mean values for 4 N, 2 N, 0·2 N, and 0·1 N acid were 90, 97, 94, and 79 mg. P_2O_5 per 100 g. soil, respectively. The lower value from the 0·1 N acid can be attributed to incomplete extraction of the released organic P. In this connexion, it can also be noted that in some cases the residues were re-extracted with fresh acid. The differences between the ignited and unignited soil, i.e. the amounts of additional organic P, in the second extracts are of the order of 0–10 mg. P_2O_5 per 100 g. soil, and are in most instances of very doubtful significance.

Effect of ignition temperature (*Table 7*). Ignitions for 1 hour at four temperatures were compared on four soils using the standard overnight extraction with 0·2 N H_2SO_4. The results show that there is little variation with temperature in the range 400–650° C., but at 800° C. the organic P values are very much lower. The very low values at 800° C.

are presumably due to volatilization of phosphate. But in the normal method it is clear that the ignition temperature is not a critical factor.

TABLE 7

Effect of Ignition Temperature on Organic Phosphorus Values, using 16½*-hour extraction with* 0·2 N H_2SO_4*—mg. organic* P_2O_5 *per 100 g. O.D. soil*

Sample no.	*Ignition temperature*			
	400° C.	*550° C.*	*650° C.*	*800° C.*
A 31492*	135	133	135	2
3 A	187	188	194	54
A 31502*	156	158	169	9
A 31496*	235	230	236	50
Means	178	177	183	29

* See footnote, Table 6.

General Discussion

The present results demonstrate the uncertainties involved in organic P estimations and the difficulty of proving conclusively that the values are correct. The usual approach [1] is to compare different methods and regard the highest value obtained as being the most likely to be correct. With alkaline extraction methods this procedure is justified because the two main sources of error, hydrolysis and incomplete extraction, both result in low values. But with ignition–acid extraction methods, there is not the same certainty, because of possible increases in the solubility of the inorganic P during ignition. It appears from Tables 6 and 7 that the experimental conditions in the Ignition method can be varied widely without any major change in the organic P values. It is particularly noteworthy that this holds for the two samples, A 31496 and 7 B, derived from slates. There is, therefore, no suggestion from the above tests that the Ignition values are too high. On the contrary, the modifications which might reasonably be introduced, such as 2 N acid and a double extraction, tend to give somewhat higher results. The possibility that in some cases there is an increase in the solubility of inorganic P during the ignition cannot, however, be ruled out. This might account for the clear differences and the apparent relationship to parent material and drainage in the case of samples 7 A, 7 B, and 7 C in Table 5, and for the rather poor agreement on subsoils 3 C, 3 D, and 3 E. But from the tendency for the Ignition values to increase when the conditions are made more drastic and the fact that the main sources of error in alkaline extraction methods make for low values, it seems much more likely that the differences between the two methods are due to the NaOH values being somewhat low. In that case, the salient factors governing the larger differences that occur in the well-drained slate and basic igneous profiles are probably firmer binding of organic P by mineral constituents and/or greater retention of readily hydrolysable forms, resulting in less complete extraction and/or greater hydrolysis. In keeping with this, other data

show that the samples from these profiles have higher phosphate retention capacities and exhibit a generally more extreme and complex behaviour towards phosphate than any of the other soils.

The results in Tables 1 and 2 emphasize the importance of an adequate acid pretreatment in alkaline extraction methods, but the values obtained by the NaOH procedure using 4 N HCl point to the necessity for guarding against hydrolysis in the acid pretreatment as well as the alkaline extraction. With increasing severity of acid pretreatment a point is probably reached beyond which increased extraction of organic P is more than counter-balanced by hydrolysis. Such considerations show that there is scope for further testing of extraction conditions, particularly with respect to the use of successive extractions of increasing severity, employing various combinations of acid treatments and alkaline extractants. Further work on these lines is in progress and it can be mentioned that none of the modifications of the NaOH method which have so far been tried has given any material increase in the organic P values. These tests are being carried out in conjunction with an investigation by chromatographic and other methods into the forms of organic P in different soils. Without adequate knowledge of the nature and properties of the individual compounds present, it is hardly possible to be certain of the validity and significance of organic P estimations by different methods. Of particular value would be quantitative separations of the individual forms. Failing this, identification of the compounds present coupled with considerations of their solubility and stability in acids and alkalis should clarify the position, particularly with respect to the possible occurrence of readily hydrolysable forms.

The immediate objective in the present work was to assess the validity of the Ignition values as estimates of the levels of organic P which were required as part of a study of the influence of parent material and drainage conditions on the distribution of phosphorus in the different profiles. The results in general, and particularly the fact that the NaOH method, which is of a markedly different type, gives in most instances closely similar values, provide very strong justification for accepting the ignition values as valid estimates. The results by the NaOH method can be regarded as minimum values. The distribution of organic P in the soils will be discussed in conjunction with other categories of phosphorus in another paper, but it is clear that both methods give essentially the same general picture. On the present soils, the Ignition method provides a simple and rapid means of estimating the total organic P, and is very suitable for routine use in characterizing soils for pedological studies and in relation to field experiment work. But alkaline extraction methods, although much more laborious, provide a more direct estimation because the organic P is determined after extraction from the soil. From this point of view they can be expected to have a wider application. With highly sesquioxidic soils, for example, even repeated extraction with 2 N H_2SO_4 may not fully recover the phosphate released during ignition and the organic P values may be much too low. In such cases, the NaOH method provides a very valuable check, because if an alkaline extraction method gives higher values than an ignition method,

it is usually certain that the latter is too low. Where a variety of soil types is concerned, some testing of experimental conditions and comparisons between the two types of method is desirable before deciding on a method for general use.

In conclusion, it should be mentioned again that the Pearson hot-ammonia extraction, Table 1, gives results which are much too low, and is much inferior to cold 0·1 N NaOH. It can also be added that extractions by the NaOH method have shown that all the organic P in some of the present soils is not oxidized by prolonged treatment with H_2O_2. This is in keeping with the known resistance of phytin to H_2O_2 [8] and illustrates the limitations of methods based on this reagent.

Summary

1. The validity of Total Organic P values measured as the increase in Inorganic P extracted by 0·2 N H_2SO_4 following ignition of soils at 550° C. has been tested by examining the effects of varying the experimental conditions and comparing with values obtained by extraction with 0·5 N NH_4OH and 0·1 N NaOH after different acid pretreatments. The soils used represent horizons from seven profiles covering the four main soil associations in north-east Scotland.

2. The results by hot-ammonia extraction are markedly dependent on the acid pretreatment, but irrespective of this, the values are much lower than by the Ignition method. Tests covering successive extractions with different concentrations of ammonia, and the effect of temperature, show that the main causes are incomplete extraction and hydrolysis of Organic P.

3. Parallel tests show that 0·1 N NaOH is much superior to 0·5N NH_4OH as an extractant for Organic P. The NaOH values are also subject to hydrolysis, and cold extractions are preferable. The values again depend on the acid pretreatment.

4. Organic P values by the Ignition method are little affected by wide variations in the ignition temperature, concentration of acid, and period of extraction. The modifications which might reasonably be introduced, such as double extraction with 2 N acid, tend to give slightly higher values.

5. Comparisons between the Ignition method and a double extraction with cold 0·1 N NaOH following pretreatment with hot 0·1 N HCl show that the values on the whole are very similar and the agreement for seventeen out of twenty-three samples is very satisfactory. But there is a tendency for the Ignition values to be slightly higher and in the case of three samples from a well-drained profile derived from slates the NaOH values are clearly lower.

6. The sources of error, relative advantages, and range of application of the two methods are discussed. The most probable explanation for differences between them is that the NaOH values are liable to be somewhat low due to incomplete extraction and/or hydrolysis of Organic P. But both methods give the same picture of the distribution of Organic P in the soils, and the results by the NaOH method can be regarded as

minimum values. The Ignition method, which is very simple and rapid to carry out, gives valid results and is very suitable for characterizing soils in pedological studies and fertility investigations.

7. All the topsoils contain large amounts of organic P, but the values are much lower and fall more abruptly in the poorly drained compared with the freely drained profiles. The implications of this and other aspects of the Organic P distribution in the soils will be discussed in a forthcoming paper in this Journal.

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A NOTE ON BASALT SOILS IN BRITAIN AND AUSTRALIA

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A recent visit to Britain enabled the writer to make a number of field observations on the soils and vegetation in relation to conditions in Australia. Although many of these observations are too incomplete to be of much value on their own, a few of them seem to be of sufficient interest to merit reporting at this stage. The soils formed on basalt are a case in point.

Under conditions of increasing precipitation in New South Wales, the climatic sequence of soils on basalt is chernozem, chocolate soil, transitional krasnozem, and krasnozem, with alpine humus soils under colder conditions in the alps and subalps (cf. Hallsworth *et al.*, 1952). Apart from some of the poorly drained, low to medium rainfall areas of Victoria, where solodization becomes a complicating factor, this type of sequence is rather general in eastern Australia.

The properties of the chocolate soils considered to be sufficiently important to warrant their separation from the brown earths as another great soil group include the heavier texture with characteristic hard, crumb- to nutty-structured, friable topsoil and cloddy subsoil, the greater abundance of montmorillonitic clay, and the higher exchange capacity. This superior (more permanent) structure and friability is also associated with a seasonally warmer or drier climate or with fairly free drainage, as would allow the soil to undergo periodic drying out.

The krasnozem profile typically shows a very friable, porous, excellently crumb-structured, brownish red to dark red clay or clay loam topsoil merging gradually into a friable, well crumb-structured (although more compact) dull crimson clay extending into the decomposing parent material below. The transitional krasnozem is intermediate to the krasnozem and chocolate soil in profile morphology, as also in chemistry and mineralogy (cf. Hallsworth *et al.*, 1952).

Under cool temperate conditions with a more uniformly distributed rainfall and lower evaporation, the usual condition in Britain is for brown earths to develop and to persist until they are replaced by blanket bog peats, the latter soils being partly relic formations. On closer inspection, however, some of these basalt areas are also found to contain minor occurrences of soils which on morphological grounds are referable to the chocolate soil, transitional krasnozem, and krasnozem groups.

Thus, on Skye, most of the peat-free basalt slopes which are only moderately well drained and remain moist for most of the year give rise to brown earths, but locally on better drained sites there are formed soils of characteristic friability and crumb to nutty structure in the topsoil, but with a more massive and cloddy subsoil, that are morphologically similar to the chocolate soils of Australia (e.g. near the Old Man of

[1] Comments by Professor E. G. Hallsworth and Mr. F. R. Gibbons are gratefully acknowledged.

Storr, Snizort, the Quirang). In a few localities the brown earths are replaced by more strongly leached soils of improved friability and redder colour in the subsoil, which resemble transitional krasnozems. Both the chocolate- and transitional krasnozem-like soils appear to be forming at the present time and to be in equilibrium with their environment; although it was noted that soils resembling transitional krasnozems may also be produced from rather strongly weathered basalt following the removal of overlying peat (e.g. between Drynoch and Glenbrittle), in which case it seems necessary to postulate a period of fairly vigorous basalt weathering prior to that of peat formation.

Somewhat smilar soil conditions are found on the basalts of Northern Ireland. Large areas of the Antrim Plateau are peat-covered, and as drainage improves along the plateau margin and on less elevated land nearer Belfast, brown earths are encountered on an extensive scale (cf. Brown, 1954). Under special topographic conditions, however, the brown earths are replaced locally by gley, prairie-like, and chocolate-like soils: the chocolate-like soils are restricted to the best drained sites; brown earths extend over most of the catena; gley soils occupy the wet lower positions, with smaller occurrences of prairie-like soils where conditions are locally drier.

Related to the chocolate soils and transitional krasnozems by increasing intensity of weathering, the krasnozems are by no means confined to tropical or even subtropical climates, as their former name of tropical red loam suggests: given an easily weathered parent material rich in bases and iron-bearing minerals, their range is extended to cool temperate environments (e.g. Tasmania; cf. Stephens, 1950). It is quite possible, therefore, that although the British environment generally is not suitable for krasnozem formation, a particularly favourable combination of conditions might be developed locally under which krasnozem-like soils could be formed. Such is the case in Glenariff in Northern Ireland, where the slopes are steep, well-drained, and thus favour vigorous weathering, and the weathering power of the mild, moist climate, moderated by the Gulf Stream, is further enhanced by the protected nature of the glen and the luxuriant vegetation of oak forest. The resultant soils, which are red in colour, friable, porous, and well-structured, are morphologically similar to krasnozems.

It is hoped that this note on the recognition in Britain of certain basaltic soils which are morphologically similar to the chocolate soils, transitional krasnozems, and krasnozems of Australia, may encourage such chemical investigations as are necessary to substantiate the writer's field interpretations.

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PROFILE DEVELOPMENT IN THE SAND DUNES OF CULBIN FOREST, MORAYSHIRE

I. PHYSICAL PROPERTIES

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Summary

Changes in some physical properties of the sand dunes of Culbin Forest, Morayshire, brought about by fixation and afforestation of the sand, have been studied on sites ranging from bare sand to mature plantations. Trees appear to be having no measurable effect on the mechanical composition of the sand apart from the deposition of litter, but studies of soil moisture and temperature, using gypsum moisture blocks and thermistors, have shown that, while the moisture content of the unplanted dunes remains comparatively high throughout the growing season due to their coarse texture, the growth of trees dries out the sand considerably, although the total moisture-holding capacity of the upper soil layers in the older stands is greatly increased by the incorporation of organic matter. The artificial fixation of the dunes by means of brushwood ('thatching') has been found to be an efficient method of conserving soil moisture.

Introduction

Culbin Forest covers an area of some 6,000 acres of aeolian sand dunes on the south coast of the Moray Firth, between the rivers Nairn and Findhorn. Their inland edge is separated by a narrow strip of agricultural land from the prominent 25-ft. raised beach which runs parallel to the coast, and corresponds at this point to the 50-ft. contour. The origin and topography of the dunes have been explained by Steers (1937), and their mineralogical composition by Mackie (1896). Details of the methods of sand fixation and afforestation practised by the Forestry Commission since the acquisition of the area in 1921 have been given by Annand (1928). Ovington (1950) investigated some physical and chemical changes occurring in the sand in plantations of Corsican pine (*Pinus laricio*) up to 20 years old, and the object of the present work was to extend these investigations to include as wide a variety of tree species and age-classes as possible, while still confining them to the true dune system of the northern and eastern parts of the forest, where the instability of the sand and the lack of moisture and nutrients constitute major obstacles to the successful afforestation of the area.

Layout of Sample Plots

Seven sample plots, 20 ft. square, were laid out on the following sites:

Plot A. Compartment 106a

Naturally fixed *Ammophila* dune, the vegetation consisting chiefly of *Ammophila arenaria*, *Carex arenaria*, and frequent small clumps of heather (*Calluna vulgaris* var. *hirsuta*), associated with *Polytrichum piliferum* and lichens. There is a thin layer of extremely dry sand

approximately ½ in. thick directly below the lichen-moss cover where this is present, but there is no visible profile differentiation.

Plot B. Compartment 107

Corsican pine, age 12 years, spaced at 4½-ft. centres, 8 to 12 ft. high, associated with large isolated bushes of broom (*Sarothamnus scoparius*) and frequent *Ammophila* clumps. Mosses and lichens are considerably more abundant than on the open dune. Pine needles form a thin but almost continuous surface cover. An extremely thin layer of grey sand is visible under some of the larger moss clumps; otherwise there is no visible profile differentiation.

Plot C. Compartment 107

Corsican pine, age 22 years, 1,670 trees per acre, mean height 29 ft. The ground vegetation is very sparse; broom, heather, and *Ammophila* are represented only by isolated suppressed plants. The sand surface is covered with a continuous carpet of Corsican pine needles, under which is a ¼-in. layer of raw humus mixed with sand grains, whose lower surface is pale grey. No visible profile development occurs below this depth.

Plot D. Compartment 176

Corsican pine, age approximately 45 years, 453 trees per acre, mean height 44 ft. Characteristic woodland species appear in the ground vegetation, e.g. *Goodyera repens*, *Hylocomium splendens*, *H. triquetrum*, and *Hypnum schreberi*. The mosses form an almost continuous thin covering over the surface. The raw humus layer is ½ in. thick, and rests on a ¼-in. layer of grey sand mixed with humus material. The sand below this layer is faintly bleached to a depth of 2 in.

Plot E. Compartment 171

Scots pine, age approximately 80 years, 396 trees per acre, mean height 40 ft. The ground vegetation is similar to plot D, but the smaller quantity of litter on the surface is marked. The soil profile is also similar, but the raw humus layer is 1½ in. thick, and is sharply differentiated from the underlying sand.

Plot F. Compartment 176

An open stand of birch (*Betula pubescens*), age approximately 40 years, 200 trees per acre, mean height 12 ft. The site is too dry for satisfactory growth of birch, whose natural habitats at Culbin are the fringes of the seasonal 'winter lakes' and drying loch beds. The ground is covered by a deep carpet of mosses and liverworts (*Pellia* spp.) averaging ½ in. in thickness. The upper ½ in. of the profile consists of a poorly decomposed brown F layer, chiefly in the form of a felted covering of birch leaves. Beneath this is a 1½ in. layer of pale grey sand, mixed at its upper edge with humus material, and merging gradually into pale yellow sand.

Plot G. Compartment 105c

A recently mobile dune, which was fixed by 'thatching' with a continuous cover of Corsican pine branches (about 4 tons per acre) the

previous year, and planted with young pine at 4½-ft. centres. Natural vegetation is almost entirely absent, and there is no visible profile development.

The Effect of Tree Growth on the Mechanical Composition of the Sand

Method

The high dune system of Culbin Forest is composed of over 99 per cent. of coarse and fine sand, and it is therefore difficult to draw conclusions as to differences in mechanical composition by applying the size grading normally used for classifying soils. In the present investigation dry sieving has been used, with a set of six 8-in. diameter B.S.S. wire-mesh sieves, so graded as to obtain a sufficient number of fractions for an analysis on a valid statistical basis. The results from each sample were expressed as a cumulative frequency table, from which were calculated the median grain size and the percentage of material less than 0·104 mm. in diameter; these two parameters were used to characterize the sample in the subsequent analysis.

In order to determine the effect of tree growth and profile development on the mechanical composition of the sand, samples were taken at three separate points in each of the plots A to G, at the surface and at depths of 6 in., 1, 2, 3, 4, and 5 ft.

Results

(*a*) *Variation of median grain size between plots*

In Table 1 plots are grouped in order of increasing median grain size, and significance levels between groups are indicated.

TABLE 1

Variation of Mean Median Grain Size between Plots

Plot	*Mean median grain size (mm.)*	*Significance level of difference*
A	0·2020	
		1·0%
F	0·2070	
E	0·2074	
C	0·2079	
D	0·2095	
		5·0%
B	0·2137	
		0·1%
G	0·2225	

The mean for plot A (*Ammophila dune*) is lower than that of any of the plots bearing trees, which, with the exception of plot B (12-year Corsican pine), fall into a group between individual members of which there is no significant difference. Plot B has a significantly higher value than this group, while the highest value of all is shown by plot G (thatch).

(*b*) *Variation of median grain size with depth*

For the plots as a whole, the mean median grain size rises from 0·1990 mm. at the surface, to 0·2028 mm. at a depth of 4 ft., falling to 0·2006 at 5 ft. Differences between means for adjacent depths, or between adjacent means when placed in order of magnitude, are not significant. There are, however, differences between plots in the effect of depth. Plots A, C, D, and F show increases in median particle size with depth up to and beyond the 1 ft. level, while in plots G, B, and E there is little indication of any trend. The mean values for these two groups are given in Table 2.

TABLE 2

Variation of Mean Median Grain Size of Groups of Plots with Depth

	Group mean median grain size (mm.)	
	Group 1	*Group 2*
Depth	*Plots A, C, D, F*	*Plots G, B, E*
0 in.	0·1975	0·2129
6 in.	0·2003	0·2160
1 ft.	0·2068	0·2116
2 ft.	0·2103	0·2119
3 ft.	0·2105	0·2186
4 ft.	0·2103	0·2148
5 ft.	0·2103	0·2090

(*c*) *Variation in percentage of finest material* ($< 0{\cdot}104$ *mm.*) *between plots*

In Table 3 plot means are grouped in order of increasing percentages of finest material, and the significance of differences between groups is indicated.

TABLE 3

Variation in Mean Percentage of Finest Material Between Plots

Plot	*Mean percentage of finest material*	*Significance level of difference*
E	0·26	
		1%
G	0·39	
B	0·41	
		0·1%
A	0·58	
F	0·59	
C	0·66	
D	0·71	

These percentages show similar variations to those given in Table 1, with unplanted plots falling into the same groups as those bearing trees.

(*d*) *Variation in percentage of finest material with depth*

Table 4 shows the effect of depth on the percentage of finest material in the plots as a whole.

TABLE 4

Variation in Percentage of Finest Material with Depth

Depth	*Mean percentage of finest material*	*Significance level of difference*
0 in.	1·85	
		0·1%
6 in.	1·14	
		0·1%
1 ft.	0·77	
2 ft.	0·71	
3 ft.	0·72	
4 ft.	0·69	
5 ft.	0·72	

The percentage of finest material decreases significantly from the surface to the 6-in. depth, and from there to 1 ft. Differences below this depth are not significant.

Although all plots follow approximately this general pattern, the actual variations in the percentage of fine material with depth are not the same in all the plots. As in the case of median grain size, plots can be grouped according to the way in which the percentage varies with depth. Mean percentages at different depths for individual plots, grouped in this way, are shown in Table 5.

TABLE 5

Variation of Percentage of Finest Material of Groups of Plots with Depth

	Mean percentage of finest material						
	Group 1				*Group 2*		
Depth	*Plot A*	*Plot C*	*Plot D*	*Plot F*	*Plot G*	*Plot B*	*Plot E*
0 in.	1·17	1·86	2·58	2·32	0·83	0·46	0·56
6 in.	1·22	1·15	0·70	0·53	0·52	0·34	0·27
1 ft.	0·60	0·58	0·46	0·56	0·29	0·34	0·29
2 ft.	0·39	0·48	0·46	0·36	0·32	0·51	0·20
3 ft.	0·39	0·36	0·43	0·39	0·35	0·39	0·14
4 ft.	0·36	0·30	0·31	0·36	0·32	0·42	0·25
5 ft.	0·31	0·47	0·55	0·34	0·22	0·41	0·40

Conclusions

The plots have been shown to fall into two groups covering not only the variation of grain size with depth (Table 2) but also the distribution of the finest material at several depths (Table 5). The increase of fine material at the surface of all plots is to be expected in a stabilizing dune

system; Bagnold (1941) has discussed the effect of wind velocity on sand movement, and has shown that topographical irregularities cause a deposition of fine material. In the absence of an A_0 horizon, thatch and *Ammophila* (plots G and A) are able to accumulate at least as much fine material as 12-year Corsican pine (plot B) in this way. If there were any appreciable mechanical action on the sand as the result of afforestation other than by deposition of organic matter, plot B could be expected to contain at least more fine material than plot G, which less than a year before the beginning of the investigation was bare, mobile dune. Further, plot E, which has been under a tree crop for 80 years, would show a considerably higher proportion of fine material than it does.

The large proportion of fine material at the surface of plots C, D, and F is consistent with the view that an A_1 horizon is being formed by downward percolation of organic material from the relatively well-developed A_0 horizon. The poor development of an A_1 horizon under Scots pine (plot E) is further illustrated by the profile description, which notes the sharp division between a thick A_0 horizon and the underlying sand. The lack of any significant differences in the content of fine material between plot A (*Ammophila* dune) and plots C, D, and F, and the fact that plot A has the smallest median grain size of any plot, also supports the view that differences in the mechanical composition of the sand in the absence of organic matter are topographical.

The Effect of Tree Growth on Soil Moisture and Temperature

The average annual rainfall in the Culbin area is 23·9 in. (Nairn), and extended dry periods in early spring are common. On the high dunes, the permanent water-table is far below the rooting depth of the trees, and moisture may therefore be considered a limiting factor to tree growth.

In order to obtain a continuous record of soil-moisture fluctuations in the sample plots over an extended period, gypsum electrical resistance blocks were used, of the cylindrical pattern proposed by Slater (1942). Thirty-two blocks were constructed, and buried at depths of 3 in., 9 in., 18 in., 3 ft., and 5 ft. in plots A to F, and at 3 and 9 in. in plot G (thatch). These depths were chosen to cover the surface layers of sand, the rooting zone of the trees, and the deeper horizons relatively unaffected by tree roots.

Bouyoucos and Mick (1947) have shown that the range of sensitivity of gypsum blocks is from a little below field capacity to a point somewhat above the wilting-point, a narrow zone characterized on the moisture-content block resistance curve by a sharp rise in resistance. The mechanical composition of Culbin sand is such that the range of moisture content between these two values is extremely small; field determinations in areas where the sand was not mixed with humus material gave a field capacity of 5–6 per cent., and a wilting-point of 0·5 to 0·9 per cent. A preliminary block calibration curve by the rapid method of Kelley (1944) showed that they could not be used quantitatively under these conditions; they were, however, well suited to the qualitative detection

of soil-moisture movement, i.e. to determine whether a particular soil horizon was at or near field capacity, or approaching the wilting-point. Used in this way, errors due to hysteresis (Croney, Coleman, and Currer, 1951; Tanner and Hanks, 1952) or temperature (Bouyoucos and Mick, 1947; Slater and Bryant, 1946) need not be considered. Uniformity of block response was checked by taking their saturated resistance when immersed in distilled water under slight vacuum (Tanner, Abrams, and Zubriski, 1948).

A total of 2,600 daily block readings were taken in all plots over two periods, the first covering April and May 1952, when the sand under trees might be expected to show signs of drying out after the winter, and the second in July and August, when any drought conditions would have reached a maximum. The results showed considerable differences between the open dunes and the tree plots. The sand under thatch (plot G) remained at field capacity throughout the period, while under *Ammophila* (plot A), although drying was detectable in all layers at intervals throughout the period, the wilting-point was only reached in one layer (3 ft.) in the middle of August. Under the 12-year Corsican pine, however (plot B), the 18-in. layer was at the wilting-point at the beginning of April, and the 9-in. layer dried out at the end of May. Both these layers remained dry until the end of August, although the moisture in the horizons above and below them fluctuated with the rainfall. The 22-year Corsican pine (plot C) behaved in a similar way, except that the dry zone extended to 3 ft. by the middle of May, where it was maintained until the end of the period. The 45-year Corsican pine (plot D) showed distinctly less drying; although the 3-ft. layer was dry throughout the period, the moisture status of the other layers was maintained above the wilting-point during the dry period in May, and there was little change in July and August. The 80-year Scots pine (plot E), the oldest plot studied, was also the driest. With the exception of the surface, the whole profile was at or near the wilting-point throughout April; thereafter some surface fluctuations were detectable, but dryness below 18 in. continued until the end of the period. The birch (plot F) behaved in a similar way to plot C, but the 3- and 9-in. layers were wetter throughout the period than those in any other plots bearing trees.

In order to confirm the gypsum block readings, quantitative measurements of soil moisture in the sample plots were made in July and August 1952. The correlation between soil moisture and root density is shown in Fig. 1. The root density given here is the air-dry weight of roots contained in a 6-in. cube of soil at the depth shown, and is the mean from three separate pits in each plot. The spread of the determinations was relatively large, and the value given is only intended to indicate the trend of rooting habit. The soil-moisture determinations were made with a 'Speedy' moisture tester, a portable instrument which records the pressure of gas released from powdered calcium carbide mixed with the moist soil (Croney and Jacobs, 1951).

Fig. 1 shows particularly that the profile under thatch (plot G) is wetter at all depths than the *Ammophila* dune (plot A), although the high readings at 1 and 2 ft., considerably above the field capacity, are

due to rainfall on 30 and 31 July. All the profiles under trees exhibit critically dry layers at depth, but the upper layers of plots C, D, and F

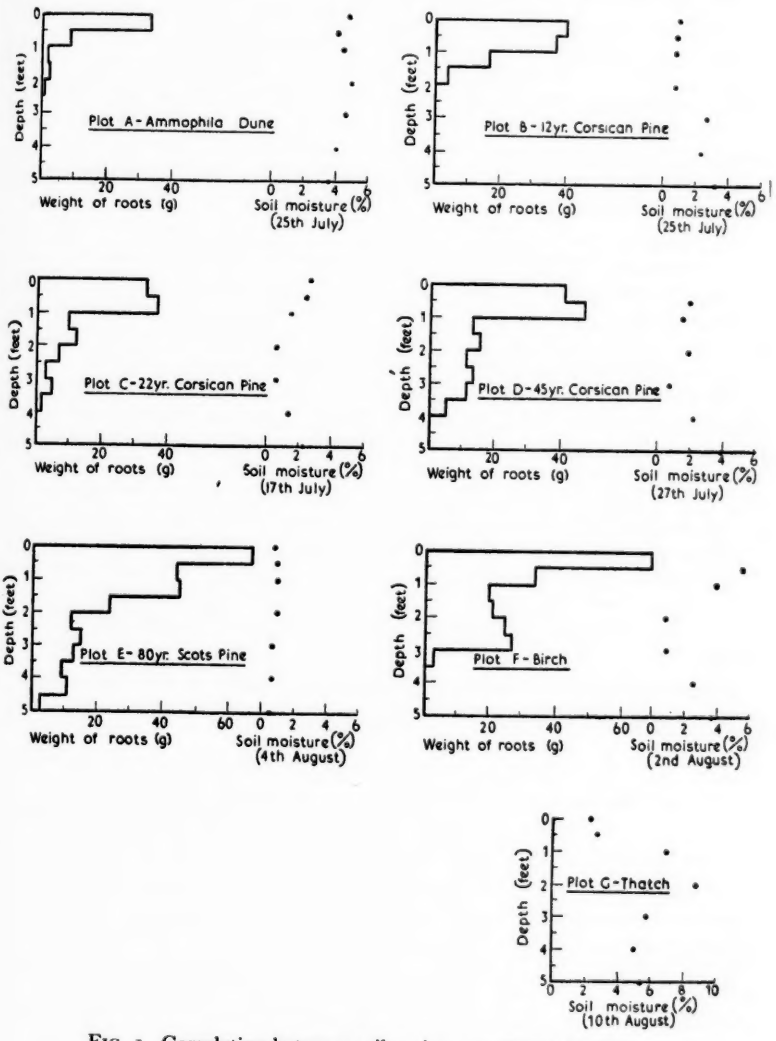
Depth (feet)
Plot A - Ammophila Dune
Weight of roots (g)
Soil moisture (%) (25th July)
Plot B - 12yr. Corsican Pine
Plot C - 22yr. Corsican Pine (17th July)
Plot D - 45yr. Corsican Pine (27th July)
Plot E - 80yr. Scots Pine (4th August)
Plot F - Birch (2nd August)
Plot G - Thatch (10th August)

FIG. 1. Correlation between soil moisture and root density.

are kept moist, due to the increase in moisture-holding capacity of the sand by the presence of organic matter. Under the older Scots pine (plot E), competition for moisture is so great that the whole profile dries out.

The influence of thinning grade on soil moisture

When a compartment is thinned, the equilibrium hitherto prevailing in the soil between rainfall, percolation, and the combined effects of evaporation and transpiration is upset. Under British conditions the normal result will be an increase in soil moisture, but it was thought quite possible that in the unusually dry climatic conditions prevailing at Culbin, thinning, by exposing a large area of the soil surface to insolation and evaporation, might be aggravating the already critical lack of moisture.

To determine soil-moisture content in similar areas bearing tree crops of different thinning grades, sites were selected as follows:

(i) Forestry Commission Sample Plot S. 186, a plot 0·302 acres in area, consisting of Quality Class II Corsican pine, 29 years old, and situated on the 'high' dunes near Lady Culbin, an area similar in topography to the plots already described. The thinning grade in this plot is C/D, and its moisture status was compared with that of the adjacent compartment 73, thinned on approximately a C grade.

(ii) Plots S. 139 and S. 140, 0·300 and 0·277 acres in area respectively, bearing Scots pine aged 31 years. Plot S. 139 has been thinned to an A grade since 1948 (previously C/D), and is in Quality Class II, while plot S. 140 has been thinned to a C/D grade throughout and is in Quality Class I. These two plots are situated in Compartment 53 in Low Wood, an extensive flat sandy area on the southern edge of the forest, between the high dunes and the 25-ft. raised beach, with a fluctuating and seasonally high water-table. They are thus not directly comparable with the other plots, but they can be compared with each other, since they lie side by side in a flat sandy area with only very small variations in microrelief.

Crop measurements in these areas are given in Table 6.

TABLE 6

Crop Measurements in Moisture Sampling Areas

	Plot S. 139	*Plot S. 140*	*Plot S. 186*	*Compt. 73*
Species . . .	Scots pine	Scots pine	Corsican pine	Corsican pine
Quality Class . .	II	I	II	II
Age (years) . .	31	31	29	29
Thinning grade .	A	C/D	C/D	approx. C
Stems per acre . .	1,387	455	579	1,070
Mean height (ft.) .	30½	41½	45	40

Soil moisture was determined by means of the 'Speedy' tester on the 15th and 16th August 1952. Three pits were dug diagonally across each plot, and samples taken at 6-in. intervals to a depth of 4 ft.; in the case of Compartment 73, the three pits were sited randomly between the rows of trees adjacent to plot S. 186. The results are given in Tables 7 and 8.

These show that in the Scots pine plot the A grade thinning is drier

TABLE 7

Variation of Moisture Content with Thinning Grade—Scots Pine

Depth (ft.)	Moisture content (% by weight)					
	Sample plot 139. A grade			Sample plot 140. C/D grade		
	SE. corner	centre	NW. corner	SE. corner	centre	NW. corner
0	8·6	4·35	3·65	5·9	7·2	4·1
½	0·4	1·0	0·9	2·3	7·4	5·25
1	0·65	0·85	0·55	1·6	3·25	6·9
1½	0·65	0·7	0·6	6·25	5·2	9·2
2	0·65	0·45	1·4	6·5	5·6	2·7
2½	3·5	3·55	1·95	4·65	0·95	1·4
3	1·7	3·0	1·35	3·8	2·9	3·0
3½	3·6	1·9	2·4	4·9	3·8	3·9
4	5·2	4·15	3·65	5·05	4·8	4·6

TABLE 8

Variation of Moisture Content with Thinning Grade—Corsican Pine

Depth (ft.)	Moisture content (% by weight)					
	Plot 186. C/D grade			Compartment 73		
	SE. corner	centre	NW. corner	1st rep.	2nd rep.	3rd rep.
0	0·8	5·65	3·35	1·5	2·0	3·95
½	1·3	2·85	1·55	2·5	0·6	4·05
1	2·9	2·9	4·6	0·55	0·5	0·85
1½	2·5	2·7	4·15	0·5	0·95	0·65
2	4·55	5·55	3·55	0·65	2·7	2·45
2½	5·45	7·1	5·5	4·4	6·1	5·8
3	4·25	6·4	1·95	3·55	5·25	0·85
3½	5·25	2·8	4·65	0·55	0·7	0·4
4	5·45	2·0	1·75	0·45	0·5	0·4

from 6 in. to 2 ft., while in the case of the Corsican pine, only a slight increase in the intensity of thinning causes a marked improvement in the moisture status at depths of 1 to 1½ ft.

The influence of ground cover on soil temperature

The high temperatures which may be expected at the surface of bare sand dunes exert a considerable influence on the moisture content of the sand, causing evaporation to take place at a much more rapid rate than from a similar surface protected from direct insolation by vegetation. Penman (1949) has shown that, averaged over the whole year in the latitude of the British Isles, the evaporation from turf is only about 75 per cent. of that from an open water surface exposed to the same conditions.

Edlefsen and Anderson (1943) and Robins (1952) have shown that theoretically the movement of moisture in unsaturated soils can be explained by the application of the laws of thermodynamics, free energy for the movement of water either in the liquid or gaseous state being

supplied by solar radiant energy, and causing a net transfer of moisture from warm areas to cold. This has been confirmed experimentally by Gurr, Marshall, and Hutton (1952), who also demonstrate that when the soil is sufficiently moist to permit liquid flow, equilibrium conditions cannot be reached and continuous circulation takes place. Both theoretical and experimental evidence shows that movement of moisture by vapour transfer is considerably slower than liquid movement, but that in unsaturated soils appreciable moisture movements can take place in this way. Since the Culbin soil-bearing vegetation is in an unsaturated state during the greater part of the growing season, temperature fluctuations in the sample plots have an important influence on soil moisture.

In order to include in the temperature studies an example of the dry heath type of vegetation without trees which occurs in certain small areas of the forest, chiefly along the sides of rides and fire lines, an extra sample plot (plot H) was laid out in Compartment 181, an unplanted area where the vegetation is dominated by *Calluna vulgaris* var. *hirsuta*, 12–18 in. high, together with abundant broom, *Ammophila*, and *Carex arenaria*. Mosses, lichens, and occasional liverworts form a thick blanket over the soil surface. The soil profile is not strictly comparable with that of the other plots; the sand is slightly finer at all depths, and bands of humus staining occur down to 5 ft. It appears to be pedologically older than the 'high' dunes, having been protected from recent sand invasion by the old woods to the north and west.

Standard Telephone thermistors type F2311/300 were used as soil thermometers; the use of similar thermistors for measuring air temperature has been described by Penman and Long (1949). After calibration in stirred water over the range 0–30° C., they were installed at depths of 3, 9, and 18 in. in plots A, B, E, and H, and at 3 and 9 in. in plot G; these five plots included all the available types of cover which could be expected to control soil temperature to appreciably different degrees.

Daily readings of the thermistors were taken at the same time as those of the gypsum blocks. These showed that soil temperatures at all depths in plot H (heather) were lower than these in any other plot, and also varied less from day to day. The highest and most variable temperatures occurred in plot A (*Ammophila* dune); between these extremes, soil temperatures in plot E (80-year Scots pine) were slightly higher than in plot H and rather lower than those in plots B and G. Of these last two, the soil in plot G (thatch) was in general very slightly warmer than that in plot B (12-year Corsican pine).

The temperature of the lower soil layers in plots B and G reached the level of that of the surface soil by the end of March, but this did not occur in plots H and E until some time later, although the process was complete by July. The strong insolation of the surface soil in plot A during the day had the effect of maintaining its temperature always a little above that of the deeper layers.

As well as these daily readings of soil temperature, measurements of the diurnal fluctuations were made on the 20th August 1952. The results follow the same pattern as the daily readings; the results for the 3-in. depth are shown graphically in Fig. 2.

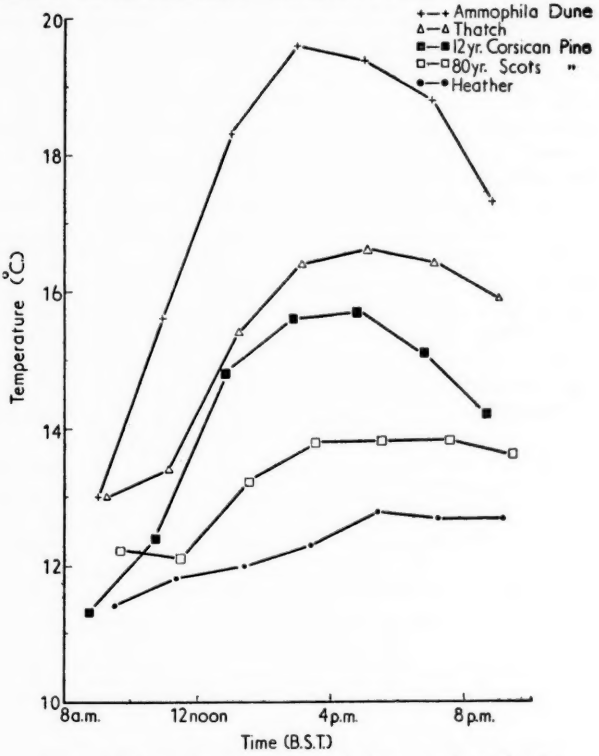

FIG. 2. Diurnal temperature variations at 3-inch depth.

Discussion

Under normal weather conditions rainfall is sufficient to keep the open dunes above the wilting-point throughout the summer. Plot A shows that the moisture requirements of *Ammophila* can be satisfied when it is present in sufficient amounts to fix the sand permanently.

The moisture distribution in plot G, Fig. 1, confirms the conclusion of Ovington (1950) that moisture falling on an unplanted dune moves down the profile as a compact mass under the influence of gravity, its upper and lower boundaries remaining sharply defined. The lower boundary is established in all soils, although textural irregularities in more normal soils cause it to be much more diffuse. Klute (1952) has shown that the sharp upper boundary is peculiar to soils with a very low field capacity. Although the moisture content of the sand through which the water mass has passed is raised to field capacity, under Culbin conditions a great proportion of any appreciable rainfall passes beyond the rooting depth of vegetation.

The abnormally coarse texture of the Culbin soil also, however, prevents excessive evaporation, since the almost complete absence of

silt and clay reduces the capillary pore space and hence limits the capillary rise of moisture caused by the application of a temperature gradient. If drying continues after the sand has been dried to the limit of the capillary rise, the consequent increase in tension finally breaks the liquid-moisture film in the smallest pores; this occurs more readily than in a soil with a more normal mechanical composition, since even the smallest pores are relatively large and hold moisture at considerably lower tensions. Further movement of moisture across the dry zone thus formed can only occur by vapour transfer, a slow process in comparison with liquid movement even under steep temperature gradients, and it has been shown that by late spring the temperature of the upper layers of soil is substantially constant. Further moisture loss thus becomes very small, the moisture level of the underlying sand remaining above the wilting-point until rainfall again wets the profile.

The maximum observed capillary rise observed at Culbin in sand devoid of organic matter was about 2 in.; the young Corsican pine transplants used to plant up the thatched dunes have a tap root of at least 3 in., and from the outset, therefore, at least part of the root system lies in a zone whose moisture-holding capacity is sufficient to meet the requirements of the crop so long as these remain small. Failure from drought in early life is not the danger which the appearance of the dunes might suggest; the usual causes are either burial by moving sand or the removal of insufficiently fixed sand from round the roots, and both of these are eliminated by adequate thatching.

The growth of trees radically alters the moisture status of the soil. Within a few years the young trees remove considerable quantities of water from the soil round their roots, although below rooting depth the soil remains at or near field capacity, the low tensions being insufficient to raise moisture to the rooting zone. During autumn and winter, rainfall may be sufficient to meet the reduced moisture requirements of the trees, although dry layers have been shown to occur at depth in the older stands even in early spring. The seasonal dry period in April and May, coupled with the onset of the growing season, causes transpiration losses to exceed rainfall in all plots bearing trees, and the soil is dried out to the wilting-point, to a depth depending on the age and rooting habit of the species. In 1952 this process was completed by the end of May, and the dry layers were not again fully wetted during the whole of the growing season.

After the closure of canopy, the incorporation of humus material into the upper layers of sand from the continuous litter layer which is formed, considerably increases their moisture-holding capacity. Although the percentage moisture content of these humose layers is many times that of the underlying sand, it appears that much of the moisture is held at tensions too high to be available to the trees, since there is no increase in the weight of roots in the surface layers of soil as the trees become older (compare plots B, C, and D, Fig. 1). Increased rooting in the A_1 horizon only occurs in the oldest plot (E) where moisture shortage has become so acute that the whole profile dries out, and where a much thicker humus layer has formed.

Under the older Corsican pine and birch the development of an A_1

horizon is sufficient to maintain the upper layers of the soil at a relatively high moisture content throughout the summer, although lower layers within the rooting depth of the trees are not prevented from drying out. Under old Scots pine, however (plot E), even the upper layers of sand become dry; the litter is not so readily incorporated into the mineral soil, but tends rather to form a thick felted A_0 horizon, sharply divided from the lower horizons, which absorbs much of the precipitation. Under all tree crops, the amount of available water in the soil decreases as the crop matures, although under species whose litter is capable of rapid breakdown the total amount of moisture retained by the upper horizons increases greatly. The available moisture under these conditions can be most efficiently utilized by adopting a heavy thinning grade.

The temperature studies show that during the early life of the trees the maintenance of surface cover is beneficial, and in particular that thatch, laid in a continuous layer less than one foot thick, has an insulating efficiency approaching that of growing trees 8–12 ft. high.

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A STUDY OF PODZOLIZATION

VI. THE IMMOBILIZATION OF IRON AND ALUMINIUM

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THE previous papers in this series have dealt with the dissolution of soil sesquioxides by tree leaf leachates. It was noted (Bloomfield, 1954*a*) that the behaviour of leachates of rimu leaves appeared to be anomalous in that under aerobic conditions the rate curve of the solution of ferric oxide shows a sudden decrease after some 10–12 days. The work described in this paper originated as a further investigation of this phenomenon, a preliminary account of which has already been published (Bloomfield, 1953).

Experimental

It was suggested earlier (Bloomfield, 1954*a*) that sorption of ferrous-organic reaction products on undissolved ferric oxide might play a part in causing the sudden fall in the concentration of dissolved iron. If this were the case it would be expected that the point at which the decrease commences would be dependent upon the amount of ferric oxide left undissolved, and that a similar process would operate in the absence of oxygen.

In order to test these assumptions, the effect of varying the ratio of ferric oxide to leaf extract was investigated. 0·5-, 0·1-, and 0·05-g. samples of ferric oxide were each treated with 200 ml. of a 5 per cent. aqueous rimu leaf extract, and the concentration of dissolved iron determined periodically in the usual manner. The experiment was carried out under aerobic and anaerobic conditions. The results (Fig. 1) show that as in the aerobic experiment, a maximum is obtained in the absence of oxygen, although it occurs later and the subsequent decrease in concentration is slower than in the aerobic system. The reprecipitation process is therefore not fundamentally one of reoxidation, although clearly the process is favoured by oxidizing conditions. It can also be seen from the figure that in both cases, the greater the amount of residual ferric oxide, the earlier the maxima occur and the more rapid is the decrease in the concentration of iron in solution, as would be the case if sorption on the undissolved ferric oxide were a determining factor.

Direct evidence for the existence of a sorption effect was obtained by allowing a ferrous-aluminium-rimu solution to percolate down a column of ferric oxide-coated sand.[1] The ferrous-aluminium solution was

[1] Acid-washed sand was moistened with a solution of ferrous sulphate and treated with ammonia solution. When the latter was present in excess, hydrogen peroxide was added. When completely oxidized, the product was washed repeatedly with tap water, then with distilled water and allowed to dry. The air-dry material contained 0·06 per cent. Fe_2O_3.

prepared by treating 0·1 g. ferric oxide and 0·02 g. aluminium oxide with 200 ml. of 5 per cent. leaf extract for *c.* 50 days in an atmosphere of nitrogen; at the time of sampling the solution curve was almost horizontal. The centrifuged solution was diluted ten times with water and aliquots were pipetted on to 10-cm. columns of wet ferruginous

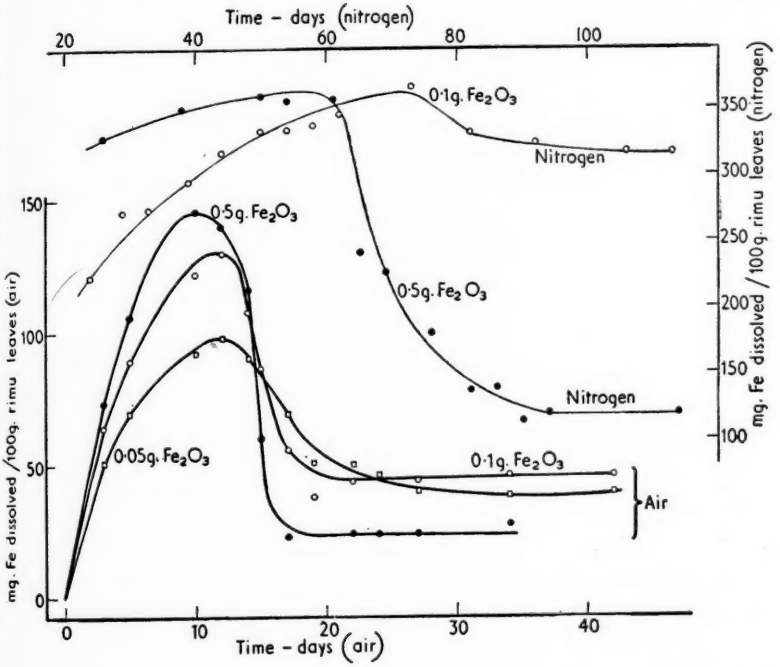

FIG. 1.

sand contained in glass tubes of 5 mm. internal diameter. The dimensions of the tubes were such that the solution was retained in the column when percolating under gravity. The iron compounds were strongly sorbed by cotton wool, paper pulp, and asbestos; the tubes were therefore plugged with glass wool which was covered by a layer of acid-washed sand.

After 2 hours the columns were washed repeatedly with distilled water (*c.* 100 ml.), suction being employed in the final stages. The iron contents of the effluents were then determined in the usual manner, with the results given in Table 1. Visual evidence of sorption was provided by the darkening of the ferric oxide and the decrease in the intensity of the colour of the solutions.

Because of the experimental difficulties associated with column experiments, the measurements were repeated under static conditions, i.e. the iron-aluminium solutions were allowed to reach equilibrium

with the sorbent, centrifuge tubes being used as reaction vessels. The results obtained after 2 hours contact are given in Table 2, from which it can be seen that with a rimu-ferrous solution on ferric oxide, in contrast to the column experiments, the net result was one of relatively extensive solution of ferric oxide. The most probable explanation of these conflicting results seems to be that sorption of ferrous-organic

TABLE 1

Sorption on Ferric Oxide Columns

	Rimu		*Scots pine*		*Larch*		*Aspen*		*Ash*	
	Fe	Al	Fe	Al	Fe	Al	Fe	Al	Fe	Al
Mg. added	0·200	0·117	0·083	0·003	0·198	0·038	0·105	0·028	0·045	0·030
Per cent. sorbed	64	53	18	66	19	13	29	39	53	52

TABLE 2

Sorption on Soil Colloids

Sorbent	Fe_2O_3	SiO_2		Al_2O_3		*Kaolin*	
	Fe	Fe	Al	Fe	Al	Fe	Al
Rimu:							
Mg. added/g. sorbent	0·189	0·345	0·562	1·394	0·583	1·730	0·592
% sorbed	−47	51	28	29	28	13	41
Aspen:							
Mg. added/g. sorbent	(n.d.)	0·525	0·140	0·525	0·140	0·525	0·140
% sorbed		Nil	Nil	40	*	29	*
Ash:							
Mg. added/g. sorbent	(n.d.)	0·225	0·150	0·225	0·150	0·225	0·150
% sorbed		33	50	56	57	9	*
Scots pine:							
Mg. added/g. sorbent	(n.d.)	0·415	0·015	0·415	0·015	0·415	0·015
% sorbed		2	7	81	33	12	Nil

* Solutions difficult to centrifuge.

compounds on ferric oxide results in the formation on the surface of the oxide particles of a relatively inert layer which inhibits further solution of the substrate. In the initial preparation of the rimu-ferrous solution this protective coating had presumably become sufficiently effective to bring the solution process almost to a standstill. In the equilibrium experiment, in which the solution came in contact with unprotected ferric oxide, rapid solution once more took place. On the other hand, in the column experiments, where unprotected ferric oxide was, in effect, continuously provided, the iron mobilizing capacity of the solution was eventually sufficiently diminished for a net sorption effect to become apparent.

If this reasoning be correct, it follows that as the rimu-ferrous solution percolates down a column of ferric oxide a net solution of the oxide would result in the top layers, while lower down, as in a podzol, a net sorption, i.e. deposition, of the dissolved iron would occur.

Because of the experimental difficulties involved in determining relatively small changes in the iron content of the ferric oxide coated sand, this supposition was tested indirectly by the following method. A rimu-ferrous solution was prepared by treating 0·5 g. ferric oxide with 200 ml. of a 5 per cent. rimu extract for 85 days in an atmosphere of nitrogen. This solution was diluted ten times for use. Quantities of

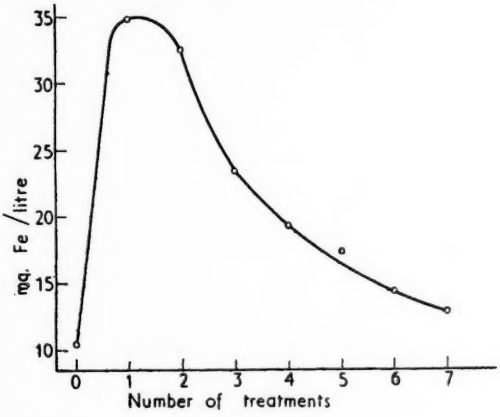

FIG. 2.

ferric oxide weighing 2·3, 2·0, 1·7, . . ., 0·5 g. were introduced into centrifuge tubes and 115 ml. of the ferrous solution were added to the first tube; the mixture was agitated for 15 minutes by a rapid stream of nitrogen. At the end of this period the suspension was centrifuged and 100 ml. of the centrifugate were added to the second tube. The process was then repeated, 85 ml. of the second centrifugate being added to the third tube, 70 ml. to the fourth, and so on down to the last tube which received 25 ml.; samples of the centrifugates were retained for analysis at each stage. Since the ratio of the weight of oxide to the volume of solution was the same for each treatment, this procedure amounts to a duplication of a column experiment in which sampling of the effluent at equal depth increments does not affect the volume of solution passing through successive layers of the column. The use of a rimu-ferrous solution instead of an untreated extract, of course, merely served to quicken the overall process.

Typical results are illustrated in Fig. 2, from which it can be seen that a rapid initial solution of ferric oxide is followed by an almost equally rapid sorption of the solution products, in direct agreement with the removal and deposition of iron down a podzolized soil profile.

It was suggested earlier that sorption of reaction products on the undissolved oxide inhibits further solution of the oxide. If this were so, addition of fresh ferric oxide should cause an appreciable increase in the rate of solution. Fig. 3 illustrates the results obtained in such an experiment, in which 0·5 g. of ferric oxide was added to a mixture containing

0·1 g. of ferric oxide and 200 ml. of a 5 per cent. rimu leaf extract which had been allowed to react in nitrogen for 38 days. The figure shows that the immediate effect of adding the fresh oxide was to cause a slight drop in the concentration of dissolved iron; this was quickly followed by a period of rapid solution which lasted for several days before giving place to a rapid decrease in concentration. During this last phase, a bulky

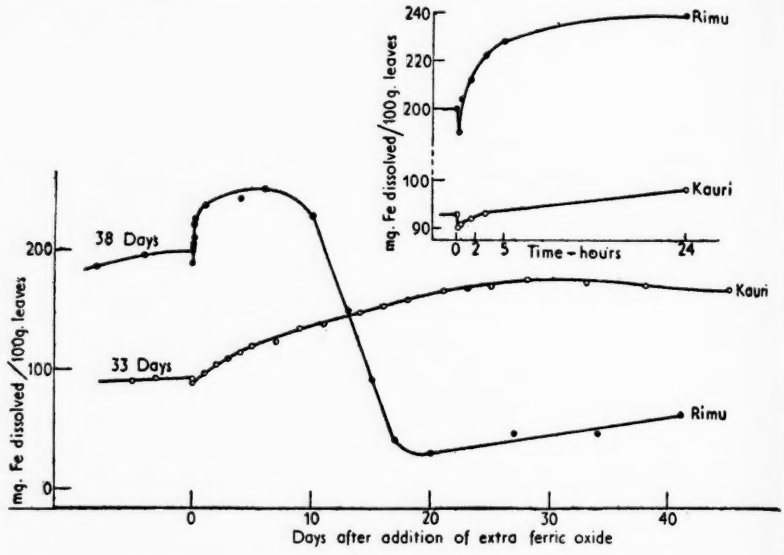

FIG. 3.

blue-black precipitate was formed, leaving the solution virtually colourless. Thus the sequence of events caused by the introduction of the additional oxide was firstly a small net sorption of iron from the solution, followed by pronounced net solution of the oxide. The final decrease in the concentration of dissolved iron is greater and occurs more abruptly than in the analogous change illustrated in Fig. 1, presumably reflecting the greater area and consequent smaller specific 'poisoning' of the ferric oxide surfaces.

Extension of this work to species other than rimu was obviously desirable. Experiments were therefore carried out to see whether kauri and larch extracts give maxima in their solution curves when allowed to react for prolonged periods with ferric oxide. These species were chosen because, in their reaction with ferric oxide, both cause intense darkening of the undissolved solid and thus give reason to suspect that sorption phenomena would be appreciable. It was found that under the conditions of these experiments (0·1 g. ferric oxide + 200 ml. 5 per cent. extract for 120 days) kauri gave no maximum under aerobic or anaerobic conditions. As previously reported (Bloomfield, 1954*b*), larch behaves anomalously, more solution taking place in air than in nitrogen; the existence of a

maximum only in the anaerobic system appears to agree with this unexpected behaviour. As there is no significant difference in pH between aerobic and anaerobic larch/ferric oxide systems, the greater solution under aerobic conditions cannot be explained by postulating the formation of acids by oxidation of constituents of the larch extract. A more probable explanation is that under aerobic conditions the ferrous complexes are oxidized to less readily sorbed ferric compounds, thus giving a greater net solution of ferric oxide.

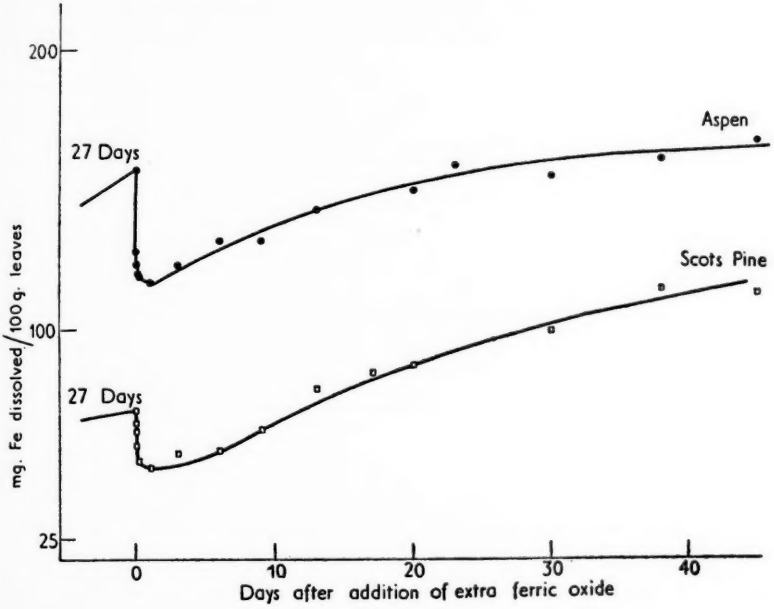

FIG. 4.

The foregoing experiments have shown that the measured concentrations of dissolved iron represent only the net excess of solution over sorption, so that it might be that maxima could be obtained in the solution curves for kauri by using relatively larger amounts of ferric oxide.

The effect of additional ferric oxide on a kauri leaf reaction mixture, illustrated in Fig. 3, shows that kauri exhibits little or no tendency to give a maximum. In other words, if the overall solution-sorption process is pictured for the moment as a reversible reaction, thus—solution $\rightleftharpoons$ sorption, in the case of the kauri system the position of equilibrium is much farther to the right than it is for the rimu system.

Fig. 4 shows the behaviour of Scots pine and aspen extract-ferric oxide systems when treated with additional ferric oxide. Consideration of these findings leads to the suggestion that the extent of sorption of the ferrous reaction products may play an important part in determining

the effectiveness of a particular species as a podzolizing agent. Accordingly an attempt was made to obtain a comparative measure of the extents of sorption on ferric oxide of the reaction products of several leaf extracts.

The ferrous-leaf extracts were prepared by anaerobic treatment of 0·05 g. of ferric oxide with 100 ml. of 5 per cent. leaf extract for 28 days. The centrifuged extracts were diluted twice with water and, as described above, allowed to percolate down columns of wet ferruginous sand. In order to investigate the effect of pH on the sorption process, the experiment was repeated after addition of dilute sodium hydroxide to the extracts. The results are given in Table 3, from which it can be seen

TABLE 3

Effect of pH on the Extent of Sorption

Ash		*Aspen*		*Oak*		*Larch*		*Scots pine*		*Rimu*		*Kauri*	
pH	% Fe *sorbed*	pH	% Fe *sorbed*	pH	% Fe *sorbed*	pH	% Fe *sorbed*	pH	% Fe *sorbed*	pH	% Fe *sorbed*	pH	% Fe *sorbed*
5·5	26·4	5·1	9·2	4·1	39·6	4·4	21·3	4·5	13·1	4·3	21·6	4·8	19·7
6·7	28·6	6·8	13·2	6·7	46·9	6·7	26·8	6·5	17·7	6·8	14·7	6·7	15·1
7·6	37·9	7·5	28·4	7·7	3·8	7·6	48·0	7·6	25·9	7·6	9·6	7·6	7·3

that for the broadleaved species a smaller percentage sorption occurred with aspen than with ash or, except for the highest pH value, with oak, which is in agreement with the relative podzolizing properties of these species. The same relationship can be seen to exist between larch and Scots pine and rimu and kauri. Rimu, kauri, and possibly oak differ from the other species in showing decreased sorption at the higher pH levels, in which respect these species resemble the grass fermentation-ferrous solutions investigated by Singh (1954). In view of the effect of increased alkalinity in promoting oxidation, it is possible that this reversal of the expected trend reflects the influence of oxidation, rather than of pH *per se*, on the extent of sorption. It is possible, of course, that the same effect operated to some extent in all these experiments.

Discussion

Attention has already been drawn to the difficulty of reconciling the relative podzolizing properties of rimu and kauri, and aspen and ash, as observed in the field, with laboratory measurements of their sesquioxide mobilizing properties (Bloomfield, 1954*a*, *b*). In addition to ash, a number of non-podzolizing broadleaved species have been found to give appreciable solution-reduction effects in the laboratory, and the

need to determine what factors operate under natural conditions to counteract the mobilization is at once apparent.

From the results of the foregoing experiments it seems that the difference between podzolizing and non-podzolizing species may, in part at least, be determined by the extent to which the mobilized sesquioxides, in the form of organic complexes, are resorbed by the soil colloids. Soil fauna, in particular earthworms, normally absent from the mineral layers of podzolized soils, no doubt play an important part in counteracting the mobilizing action of the leachates. In this connexion it is of interest to note that earthworms are not found in the podzolic grey wooded soils of central N. America (A. Leahey, private communication).

It is perhaps relevant to note that in a well-developed kauri podzol the A_2 horizon may consist largely of silica, silica sesquioxide ratios of 70 having been reported (Taylor, Dixon, and Seelye, 1950). It has been found experimentally that while leaf leachate-ferrous compounds are strongly sorbed on kaolin, chromatographic silica exerts a very much smaller sorptive influence. Removal of clay from the kauri A_2 horizon can thus be seen to favour removal of sesquioxides, and the efficiency of the kauri as a podzol former may, in large measure, be due to the weathering or transportation of clay minerals under its influence.

The extent of sorption of iron from the various leaf leachates, as indicated by Figs. 3 and 4, shows that sorption varies inversely as the efficiency of the species as a podzol former; this is in agreement with the suggestion that the podzolizing properties of a species depend on the relationship between its solution and sorption characteristics. Although the results of the column experiment agree well with this suggestion, it is not felt that too much weight should be given to these particular results. If one considers the conditions necessary for a valid comparison of the sorption characteristics of any two species, it can be seen that in the present state of our knowledge they are virtually impossible to achieve. It has been shown that sorption of reaction products takes place during the preparation of the ferrous solutions; as the extent of this sorption is not known, it is possible that the greater part of the sorbable material has already been removed from solution by the time the sorption measurements are commenced. Since the rate and relative extent of solution and sorption are likely to differ from species to species, it is clear that after equal reaction times it is unlikely that the solutions will be in comparable states for the purpose of sorption measurements.

In earlier work on the sorption of ionic ferrous iron, the results indicated that ferrous iron is more easily oxidized when sorbed than is otherwise the case (Bloomfield, 1951). The presence of organic matter has prevented a similar investigation of the effect of sorption on the ease of oxidation of the leachate ferrous complexes. If sorption has the same effect on the stability of the complexes, it would not be necessary to postulate more than partially aerobic conditions to account for their reoxidation in the B horizon, and this would, presumably, result in the formation of fresh surfaces capable of sorbing further material. The process would thus be self-regenerating.

Summary

The sorption of iron- and aluminium-leaf leachate compounds on soil colloids has been studied.

In general the extent of sorption varies inversely as the efficiency of the species as a podzolizing agent.

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GREY WOODED (PODZOLIC) SOILS OF SASKATCHEWAN, CANADA

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THE so-called grey wooded soils were first studied and described in western Canada, where they occupy many millions of acres of the forest region. They are characterized by thin A_0 horizons, thick, light greyish A_2 horizons, and brown to greyish-brown, heavier-textured B horizons. The C horizons, and sometimes the lower B horizons, are usually calcareous, although non-calcareous parent materials may also occur. Quite frequently a transitional A–B horizon is present. The A_1 horizon is very thin or absent.

In view of their early recognition and wide extent in Canada it is particularly appropriate to review the literature covering Canadian grey wooded soils, and to present some recent work from Saskatchewan. It is also important to discuss the place of these soils among the podzolic soils of the world and to deal with the problem of their classification and nomenclature.

Review of Literature

The first published descriptions and analyses of Canadian grey wooded (podzolic) soils are contained in papers by Joel (1926, 1928) and Wyatt and Newton (1928). Fertility studies of these soils were commenced in 1925, as reported by Wyatt and Ward (1929). The first work on the mapping of grey wooded soils is presented in provincial soil-survey reports (Joel *et al.*, 1929; Wyatt *et al.*, 1930).

In these first publications the soils are referred to as 'timber grey' and 'grey bush' (podzol and podzol-like) in Saskatchewan and as 'wooded' (podzol and podzolic) in Alberta. Subsequent Canadian soil-survey reports and published papers contain references to wooded, grey wooded, grey (leached podzolic), podzolic wooded, grey podzol, and grey podzolic soils. Since about 1940 most Canadian workers have referred to these soils as grey wooded. In Saskatchewan the preference has been for the name 'grey podzolic' although 'grey wooded' has also been used. It is important to realize that the early use of such names as 'grey bush' and 'grey wooded' was designed to introduce a simple term to the public (Mitchell and Moss, 1948). In the majority of technical publications and discussions these local names are qualified by references to the podzolic nature of these soils.

Since 1930 additional areas of grey wooded soils have been mapped and studied in Alberta and Saskatchewan, and this work is covered in the respective provincial soil-survey reports. Grey wooded soils were also studied in Manitoba (Ellis, 1938), the North-West Territories (Leahey, 1948), and British Columbia (Kelley and Farstad, 1946). The geographical distribution of these soils in Canada has been indicated by

Leahey (1946). It should be noted, however, that the northern boundary of the grey wooded soils has not yet been determined in all parts of Canada. In recent years these soils have also been reported from the United States (Thorp and Smith, 1949; U.S.D.A. 1952; Nygard *et al.*, 1952; Williams and Bowser, 1952).

In addition to determining the geographical location of grey wooded soils, the soil surveys and related studies have furnished knowledge of the parent materials, profile morphology, and composition of these soils. During the early years, laboratory studies were largely confined to determinations of pH, nitrogen, phosphorus, and other constituents of particular importance to soil fertility. Profile analyses which included additional constituents such as silica and sesquioxides were first reported by Joel (1928), and later by Leahey (1932), and Moss (1937). Profile analyses are also contained in Alberta and Saskatchewan soil-survey reports published since 1935.

Base-exchange studies of grey wooded soils were first reported by Holowaychuk (1932), and later by Riecken (1934), and Mitchell and Riecken (1937). Mechanical analyses were reported by Moss (1937), and studies of the forest floor by Gross (1946). Studies of clay minerals occurring in grey wooded soils of Saskatchewan were made by Warder and Dion (1952), and Brown (1952). The studies referred to above form the basis of the following statement on the composition of the grey wooded (podzolic) soils of western Canada.

The profiles of grey wooded soils, above the calcareous horizons, are usually slightly to moderately acid, but may range from slightly alkaline in the surface to strongly acid in the B horizons. The B horizons are usually the most acid of the mineral horizons. The base status is high, although this has not been confirmed for the more acid, non-calcareous profiles.

The A_2 horizons are lowest in clay, bases, and sesquioxides, and highest in silt and silica.

The B horizons are higher in clay, bases, and sesquioxides than the A_2 horizons and lower in silica and silt. The parent materials are generally slightly to highly calcareous, with lower sesquioxide and clay contents than the B horizons. The latter statement may not hold for glacial lacustrine clays, in which it is common for the total clay content to increase with depth. The clay minerals appear to be chiefly of the 2:1 layer lattice type.

There is usually a slight increase in nitrogen and organic carbon in the B horizon as compared with the A_2. This condition is not always encountered however.

The foregoing statement on the chemical nature of the grey wooded soils, together with the earlier statement on morphology, constitute a general description of these soils as a whole. To complete the general picture, it should be added that most of the grey wooded soils of western Canada occur under a mixed-wood forest in which poplar, white spruce, and jack-pine predominate on the upland, with black spruce, tamarack (larch), and willows in more poorly-drained sites (Halliday, 1937). Climatic conditions may be described as continental sub-humid and

microthermal, with a mean annual precipitation of about 15·5 in. and a mean annual temperature of 31·3° F. (McKibbin, 1948). Parent materials consist largely of calcareous glacial and post-glacial deposits overlying Cretaceous sediments. Other geological conditions may be encountered, particularly in the areas adjacent to the Rocky Mountains and in the Pre-Cambrian Shield. Agriculturally, grey wooded soils are initially less fertile and productive than the black-grey and black soils. Grey wooded soils respond to applications of ammonium phosphates, sulphur, and barnyard manure. Poor physical conditions of the plow layer and the difficulty of obtaining a good seed bed are associated with the thick A_2 horizons.

Grey Wooded (Podzolic) Soils in Saskatchewan

Studies of grey wooded or grey podzolic soils of Saskatchewan occurring on a variety of parent materials and topographic positions reveal there are a number of important types or varieties of these soils in this region. The podzolic profiles so far identified in Saskatchewan are listed and described in Table 1, together with the related degraded black soils which exhibit some features of the podzolic soils. The location of the grey (podzolic) and other major soil zones is shown in Figure 1.

TABLE 1

Principal Genetic Profiles of Podzolic Soils

Upland grey podzolic. Thin A_0; very thin or absent A_1; thick, grey to white, platy A_2; brown to greyish-brown, heavier-textured B_1 massive to weak columnar structure, breaking to hard angular, cubic, or nutty structures; light brown or yellow-brown B_2; calcium carbonate usually present, but may not occur above parent material (C_1 horizon). A transitional A–B horizon may occur in this profile.

Brownish-grey podzolic. Differs from grey podzolic in possessing grey to dark grey A_1, pale brown to brownish-grey A_2, and a brown irregular cloddy to coarse granular less compact B_1.

Grey podzolic-solonetzic. In addition to podzolic A_0 and A_2, is characterized by a solodized, columnar-structured B_1, which is heavy-textured and compact. Gypsum and other salts may appear in lower horizons.

Depression podzolic ('Bluff podzol'). Thin A_0; thick, greyish, platy A_2, with rusty or yellowish streaks. A–B horizon may be present. Dark coloured, heavy-textured B; mottled, poorly drained lower B and C (gley-like).

Peat-podzolic. Organic (peat) surface over grey, leached A_2; mottled, sticky B and C horizons.

Grey podzolic sand (podzolized sand). Thin A_0; thick to very thick, grey to brownish-grey A_2, with weak platy structure to loose structureless condition. A thick A–B horizon may occur. Brown to yellowish-brown B horizons, slightly compacted to loose and structureless. Slightly calcareous to non-calcareous parent material.

Podzol-like. Thin to moderately thick A_0; thin, light grey to pinkish-white, platy-structured A_2; reddish-yellow, yellow-brown, or brownish-yellow B horizons, which possess little structure or compaction; non-calcareous sandy parent material. These podzol-like A_2 and B_1 horizons may also occur on light-textured materials overlying a heavier-textured B_1 horizon, suggesting the formation of a podzol profile within the thick A_2 of a grey wooded soil.

Degraded black. A_0; dark grey to dark brown, granular-platy to cloddy-platy A_1; greyish-brown to brownish-grey, platy A_2; heavier-textured, coarse granular, nutty,

or columnar-structured B_1; calcareous lower B and C horizons. Both slightly and moderately degraded profiles are recognized, and degraded black-solonetzic profiles also occur.

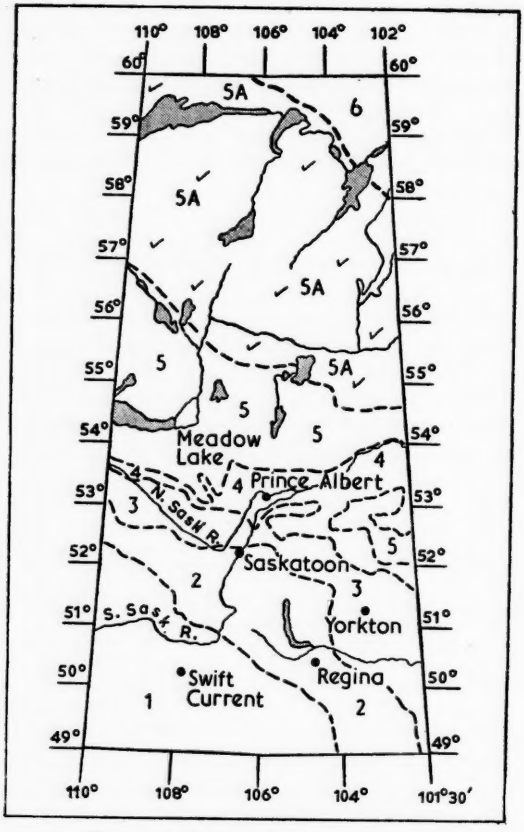

FIG. 1. Soil zones of Saskatchewan.

1. Brown soils; short-grass and mixed prairie vegetation. 2. Dark brown soils; mixed prairie vegetation. 3. Black soils; parkland (prairie and wooded) vegetation. 4. Black-grey soils; grassland-forest transition. 5. Grey (podzolic) soils; mixed-wood forest. 5A. Grey (podzolic) soils and rock outcrops; northern coniferous forest. 6. Transition podzolic-tundra soils and rock outcrops; sub-Arctic forest.

Site characteristics

The upland grey podzolic soil is the dominant podzolic profile of the surveyed areas of Saskatchewan, and corresponds most closely to the generalized description of the grey wooded soils given above. It is found on well-drained loamy, silty, and fine-textured sandy deposits.

The brownish-grey podzolic profile is most common on the lacustrine and lake-modified boulder clay deposits of the Saskatchewan Lowland, east of Prince Albert. The relation of these soils to the grey podzolic profiles is not clear. The brownish-grey profiles appear to be less podzolized than the grey wooded, and hence might be regarded as representing an earlier stage of development. However, as indicated above, these soils do not occur everywhere in the podzolic soil region, and in particular do not form a transition belt between the degraded black and grey podzolic soils.

The grey podzolic-solonetzic soils of western Canada were first encountered in Saskatchewan. They appear to represent former solonetzic profiles which have undergone a later stage of podzolic weathering. These soils occur on nearly level topography and on salinized parent materials. The depression podzolic soils are found beyond the borders of the true forest region—occurring in local wooded depressions in the black (grassland) and black-grey (grassland-forest) zones. These soils are considered to be poorly drained grey podzolic types. In the grey (podzolic) zone they are replaced by the peat-podzolic soils.

Grey podzolic sands are grey podzolic soils whose profile characteristics are influenced by sandy, slightly calcareous to non-calcareous, parent materials. These soils occur on glacial outwash and alluvial-aeolian sands.

Podzol-like and complex podzol-grey wooded soils are encountered on coarse-textured, non-calcareous sediments. These soils do not cover large areas of the settled portion of the province, and hence have not been studied to the same extent as have the dominant podzolic soils developed on calcareous glacial deposits.

The degraded black soils represent former black (chernozemic) profiles which under the influence of a later invasion of forest cover have developed some characteristics of podzolic soils.

Recent Studies of Podzolic Profiles of Saskatchewan

In 1951 it was decided to inaugurate a study of the principal genetic profiles representing the grey wooded (grey podzolic) and related black-grey (degraded) soils. Since that time eighteen profiles have been sampled and partially analysed. It is hoped to follow the preliminary analyses with more detailed studies of selected profiles. The present paper deals with the site characteristics, morphology, and partial analyses of several important types or varieties of podzolic soils. This information will assist in establishing the range in the characteristics of these soils. In addition, the information will permit further comparisons between grey wooded and other podzolic soils.

In the profile descriptions given below, the colours of the soil horizons were determined in the dry state using the Munsell colour chart. The symbol 'B_1' is applied to a main sub-horizon of the B horizon, corresponding to the B_2 as used by American pedologists. The descriptions of soil structures are those used in Saskatchewan. The soil-association names listed after each profile refer to soils established and mapped by the Saskatchewan Soil Survey.

The description of each soil profile is followed by the laboratory results. The methods of analysis are briefly described below: mechanical analysis by the pipette method, following pretreatment with HCl and H_2O_2. Sodium meta-phosphate ('calgon') was used as a dispersing agent. The fractions reported include sand (2·0–0·05 mm.), silt (0·05–0·002 mm.), clay (< 0·002 mm.), fine clay (< 0·125 μ), and International silt (0·02–0·002 mm.). The fine clay was separated by a centrifuge. The results of the mechanical analyses are reported as percentages of each fraction on a mineral matter basis, excluding organic matter and carbonates.

pH values were determined by the soil-paste method, using a glass electrode. Total nitrogen was determined by a semi-micro Kjeldahl method. Total carbon was determined by dry combustion, and organic carbon (O.C.) was obtained by correcting the total carbon for carbonates. Total analyses of silica, sesquioxides, and bases were determined by standard methods, following sodium carbonate fusion. All chemical analyses are expressed as percentages of the oven-dry soil.

Profile F4

Upland grey podzolic profile on boulder clay (Loon River Association). Site—Near Loon Lake, about 54° 3′ N. Lat., 109° 4′ W. Long. Gently undulating ground moraine. Well drained, with 1 per cent. slope to the north. Elevation 1,800 ft. Vegetation—small aspen and willow, second-growth forest (after fires).

A_0 1–0 in.	Twigs, leaves (L) with decomposing organic material (F and H layers).
A_2 0–7 in.	Light brownish-grey; platy structure, brittle when dry, crushing to loose powdery condition.
B_1 7–9 in.	Greyish-brown to dark greyish-brown with occasional greyish spots. Small cloddy to coarse granular structure, some faint platy structures evident. Heavier-textured than A_2.
B_2 9–22 in.	Greyish-brown to brown; massive, breaking to hard, cubic (blocky) and angular fragmental aggregates.
B_3 22–32 in.	Medium to dark greyish-brown; massive, breaking to small clods.
C_1 32–44 in.	Greyish-brown, with whitish streaks of calcium carbonate; moderate effervescence in dilute HCl; massive, breaking to small cloddy aggregates.
C_2 44–66 in.	Similar to C_1, but breaking to coarse granular aggregates.

TABLE 2

*Partial Analysis of Profile F4**

Horizon	*Sand* %	*Silt* %	*Clay* %	*Int. silt* %	pH	N %	O.C. %
A_0	..	..	..	..	6·1	1·98	26·80
A_2	37·5	55·8	7·1	25·4	6·4	0·04	0·34
B_1	44·9	25·4	29·7	14·0	5·7	0·05	0·40
B_2	45·7	23·8	30·5	14·7	5·5	0·04	0·30
B_3	50·2	18·4	31·9	13·1	5·8	0·03	0·26
C_1	51·3	22·0	26·4	13·3	7·5	0·03	0·12
C_2	50·5	24·1	25·4	14·0	7·5	0·03	0·06

* Analysis by M. A. Zwarich (1953).

TABLE 3

*Total Analysis of Profile F4**

Horizon	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	TiO_2 %	CaO %	MgO %	*Ignition loss* %
A_2	83·80	1·86	7·38	0·56	0·80	1·34	1·83
B_1	76·80	3·66	10·68	0·54	1·10	2·28	2·87
B_2	77·30	3·95	11·72	0·53	1·14	2·25	2·68
B_3	78·20	3·70	9·97	0·53	1·22	2·15	2·27
C_1	73·00	2·89	9·02	0·49	4·38	3·96	5·34
C_2	73·00	2·91	9·29	0·50	4·04	4·07	4·97

* Analysis by M. A. Zwarich (1953).

TABLE 4

*Analysis of Clay Fraction of Profile F4**

Horizon	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	TiO_2 %	CaO %	MgO %
A_2	43·89	4·21	12·04	0·82	0·23	2·68
B_1	49·41	8·04	19·02	0·86	0·15	3·89
B_2	50·18	8·20	18·73	0·89	0·19	3·76
B_3	52·14	7·52	17·67	0·89	0·41	3·70
C_1	52·34	7·52	16·69	0·89	0·54	4·18

* Analysis by M. A. Zwarich (1953).

Profile F4 represents the grey wooded (podzolic) soils occurring on relatively slightly calcareous clay. Table 2 illustrates the well-developed textural profile characteristic of these soils, with a concentration of clay in the B horizons and a high content of silt in the A_2 horizon. The pH values are also characteristic, the lowest values occurring in the B horizons, and the highest values in the parent material, which contains calcium carbonate. The results for nitrogen and carbon indicate a slight accumulation of organic matter in the B horizon.

Table 3 indicates a moderate movement of sesquioxides from the A to the B horizons, and a correspondingly high content of silica in the A_2. The table also shows the loss of alkaline earths from the profile, with the greatest loss occurring in the A_2 horizon. Essentially similar results have been obtained from the analysis of other grey wooded profiles occurring on calcareous glacial deposits.

The analysis of the clay fraction of profile F4, as shown in Table 4, indicates that the A_2 horizon has lost silica, sesquioxides, and bases. A very slight accumulation of Fe_2O_2 and Al_2O in the B horizon is also indicated.

Profile F13

Upland grey podzolic profile on glacial lake clay (Garrick Association). Site—Near Garrick, about 53° 28′ N. Lat., 104° 22′ W. Long. Very gently sloping glacial-lake plain occupied by lake-modified heavy boulder clay and some lacustrine deposits.

Well drained, with 1 per cent. slope to east. Elevation 1,410 ft. Vegetation—thick second growth aspen, with underbrush of hazel and dogwood.

A_0 3–0 in.	Twigs, leaves, and decomposing organic material.
A_2 0–8 in.	White; thin platy structure.
A–B 8–12 in.	Light grey; cloddy-platy structure.
B_1 12–21 in.	Greyish-brown; massive to faint columnar structure, breaking to hard cubic and angular fragmental aggregates; heavy texture, compact.
B–C 21–25 in.	Dark and light grey, faintly banded; cloddy structure; occasional streak of gypsum.
C 25–36 in.	Banded dark and light grey; massive, breaking to cloddy structure; slight effervescence in dilute HCl found in light-coloured bands.

TABLE 5

Partial Analysis of Profile F13

Horizon	*Sand* %	*Silt* %	*Clay* %	*F. clay* %	*Int. silt* %	pH	N %	O.C. %
A_0	..	..	..	..	..	6·2	1·64	26·51
A_2	33·2	50·8	16·1	3·6	30·7	5·3	0·06	0·77
A–B	44·2	26·0	29·9	14·9	14·8	4·9	0·04	0·38
B_1	9·6	20·4	70·3	37·4	17·1	4·9	0·07	0·75
B–C	1·4	21·0	77·6	33·2	19·3	6·3	0·07	0·68
C	1·2	18·6	80·2	31·1	17·9	7·2	0·05	0·06

Profile F13 represents a grey wooded soil developed on glacial lake clay. The mechanical analysis shows that the total clay content increases with depth. This is typical of heavy-textured glacial lacustrine deposits. As a result clay concentration in the B_1 is not evident from the figures for total clay. However, there is an accumulation of fine clay ($<0{\cdot}125\mu$) in the B_1 as compared to the C horizon. The sand content decreases sharply with increasing clay content, but the distribution of silt throughout the profile is characteristic of most grey wooded soils. The values for nitrogen and organic carbon indicate slight accumulation of organic matter in the B_1 and B–C horizons.

Profile F14

Brownish-grey podzolic profile on alluvial sandy-gravelly deposits (Smeaton Association). Site—Near Henribourg, about 53° 25′ N. Lat., 105° 37′ W. Long. Gently undulating alluvial upland. Well drained, with 1·5 per cent. slope to south-south-west. Elevation 1,600 ft. Vegetation—second growth aspen.

A_0 1·5–0 in.	Organic surface.
A_1 0–1·5 in.	Mixed dark grey and brownish-grey; platy-granular structure.
A_2 1·5–6 in.	Pale brown; cloddy-platy structure.
A–B 6–7 in.	Transition horizon, leaching of top of B_1, not sampled.
B_1 7–11 in.	Light brown to yellow-brown; large blocky-columnar structure, moderately compact.
B_2 11–15 in.	Yellow-brown; structure as in B_1.
C(D) 15–23 in.	Light yellow-brown gravelly sand; roughly stratified; occasional slight effervescence.
C 24–36 in.	Very pale yellow; loose, structureless; strong effervescence.

TABLE 6

Partial Analysis of Profile F14

Horizon	*Sand* %	*Silt* %	*Clay* %	*Fine clay* %	*Int. silt* %	pH	N %	O.C. %
A_0	..	..	..	..	..	6·3	1·39	23·61
A_1	54·5	36·4	9·1	5·2	16·8	6·4	0·49	6·96
A_2	57·3	33·4	9·3	4·8	12·3	6·4	0·04	0·54
B_1	41·8	33·3	25·3	16·9	12·3	5·9	0·05	0·53
B_2	48·3	31·2	20·5	13·5	11·0	6·2	0·04	0·14
C(D)	82·7	8·0	9·4	5·2	6·9	6·9	0·02	0·19
C	62·3	26·3	11·4	4·6	7·8	7·8	0·01	0·07

Profile F14 represents a variety or type of grey wooded soil that is characterized by a more brownish (stronger chroma) profile than the grey podzolic; the brownish-grey profile is also characterized by a thin but definite A_1 horizon. Otherwise, the results shown in Table 6 suggest that this profile belongs to the grey wooded group. It will be noted that there is a definite accumulation of fine clay, as well as total clay, in the B horizons. The C(D) horizon represents a more gravelly stratum containing 19 per cent. gravel ($> 2{\cdot}0$ mm.). This is not always present. It will also be noted that there is no evidence of humus accumulation in the B horizons.

Profile F12

Grey podzolic-solonetzic profile on glacial-lake clay (Arborfield Association). Site—Near Leacross, about 53° 5′ N. Lat., 104° W. Long. Very gently undulating glacial lake plain, nearly flat where sampled; moderate drainage. Vegetation—second growth aspen and shrubs.

A_0 2–0 in.	Chiefly well-decomposed organic matter (H layer).
A_1 0–1 in.	Dark grey; weak platy structure.
A_2 1–7 in.	Grey; small cloddy macro-structure, breaking easily to platy aggregates.
B_1 7–18 in.	Dark grey-brown; large blocky-columnar structure, breaking to hard angular and small blocky aggregates. Heavy-textured, compact.
B(ca) 18–29 in.	Faintly banded dark grey and brownish; massive, breaking to weak columnar structure. Moderate effervescence.
C_1 29–44 in.	Dark and lighter coloured varves. Moderate effervescence. Gypsum and probably other salts present.
C_2 44–54 in.	Appeared to be slightly less calcareous, otherwise similar to C_1.

TABLE 7

*Partial Analysis of Profile F12**

Horizon	*Sand* %	*Silt* %	*Clay* %	*Int. silt* %	pH	N %	O.C. %
A_0	..	..	..	..	..	..	..
A_1	26·4	44·0	29·6	33·3	6·4	0·21	3·08
A_2	20·9	38·0	41·1	25·8	5·6	0·09	1·02
B_1	20·3	26·7	53·0	18·2	4·8	0·08	0·68
B(ca)	5·8	29·0	65·2	24·7	7·2	0·06	0·71
C_1	4·2	27·8	68·0	22·9	7·9	0·06	0·79
C_2	0·5	26·2	73·3	17·9	7·7	0·06	0·87

* Analysis by W. K. Janzen.

Profile F12 represents a complex podzolic-solonetzic soil. The solonetzic nature of the profile is indicated by the compact, columnar-structured B_1 horizon and the variable thickness of the A horizon, which, in exposed road cuts, is shown by a 'wavy' or undulating line marking the top of the B horizon. The presence of salts in the lower horizons, also characteristic of solonetzic soils, is confirmed by conductivity measurements of the saturated soil extracts: conductivities of 4·0, 5·7, and 6·8 millimhos per cm. were recorded for the B(ca), C_1, and C_2 horizons respectively.

The podzolic nature of profile F12 is indicated by the presence of an A_0 horizon and by the fact that the lowest pH value occurs in the B_1 horizon; degraded solonetzic (solodized) soils are commonly most acid in the A_2 horizon. The high silt content of the A horizon is characteristic of both podzolic and solonetzic soils. An accumulation of clay in the B horizons is also characteristic of both soils, but is not evident from the analyses in Table 7. As stated under profile F13, soils developed on lacustrine clays tend to show increasing clay content with depth. It is very probable that a determination of the fine clay would have shown an accumulation in the B.

Profile F8

Depression podzolic ('Bluff Podzol') profile on calcareous boulder clay. Site—East of Yorkton, about 51° 11′ N. Lat., 102° 12′ W. Long. Roughly undulating ground moraine (2–5 per cent. slopes, closely spaced ridges) with general northerly slope. Profile taken in poorly drained but arable depression, slope 0 per cent. Elevation 1,745 ft. Vegetation—aspen and willows.

A_0 2–0 in.	Twigs, leaves, and decomposed organic material (L and H).
A_1 0–2 in.	Medium to dark grey; platy structure.
A_2 2–12 in.	Light grey; platy structure, crushing to loose powdery condition.
B_1 12–16 in.	Greyish-brown to brownish-grey, occasional rusty streak; weak columnar structure, breaking to cubic and angular fragmental aggregates.
B_2 16–25 in.	Dark grey-brown and yellow-brown, occasional rusty streak; massive, breaking to columnar structure.
B–C 25–28 in.	Transitional horizon, not sampled.
C_1 29–36 in.	Mixed colours—white, grey-brown, yellowish. Massive, breaking to irregular cloddy and granular aggregates; moderate to strong effervescence.

TABLE 8

Partial Analysis of Profile F8

Horizon	*Sand* %	*Silt* %	*Clay* %	*Fine clay* %	*Int. silt* %	pH	N %	O.C. %
A_1	41·9	47·2	10·8	6·0	29·5	5·7	0·23	3·12
A_2	41·8	47·3	10·7	4·8	29·6	6·0	0·08	0·84
B_1	40·7	31·5	27·9	17·0	20·6	5·7	0·05	0·38
B_2	39·2	24·9	36·0	23·8	17·6	5·9	0·05	0·40
C_1	49·9	24·1	26·0	15·9	15·4	7·5	0·04	0·49

TABLE 9

Total Analysis of Profile F8

Horizon	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	TiO_2 %	CaO %	MgO %	*Ignition loss* %
A_1	74·07	2·53	8·61	0·58	1·21	2·01	9·06
A_2	77·71	2·87	8·89	0·63	0·98	1·96	3·55
B_1	72·50	4·64	12·24	0·66	0·99	2·54	4·75
B_2	70·70	5·30	13·06	0·67	1·13	2·71	5·96
C_1	59·82	3·71	8·93	0·51	8·19	3·86	12·75

Profile F8 represents the depression podzolic or 'Bluff Podzol' soil found in upland depressions throughout the black (chernozem) and black-grey (transition) zones. Morphologically this profile is similar to the upland podzolic except for the evidence of poor drainage. The depression podzolic soils have been regarded by Saskatchewan workers as poorly drained grey podzolic (grey wooded) soils. The analytical results shown in Tables 8 and 9 support this view. The pH values and the mechanical and chemical composition of the profile show the same trends as those indicated by profile F4 (Tables 2 and 3). The main difference is the presence in the depression podzolic profile of an A_1 horizon, and the absence of any humus accumulation in the B. The high content of MgO compared to that of CaO may be noted in both profile F4 and profile F8.

Profile F11

Podzolic sand on glacial alluvial-lacustrine deposits (Sylvania Association). Site—Near McKague, about 52° 35′ N. Lat., 104° W. Long. Very gently undulating plain bordering glacial lake bed. Slope 2 per cent. to north-east. Elevation 1,750 ft. Vegetation—second growth aspen and willow.

A_0 2–0 in.	Partially decomposed and well-decomposed organic material (F, H).
A_2 0–10 in.	Very pale brown, sandy; cloddy-platy structure, crushing to loose sand.
A–B 10–18 in.	Light brownish-grey, sandy, cloddy-platy structure.
B_1 18–32 in.	Light yellow-brown; massive, breaking to weak cloddy aggregates.
B_2 32–42 in.	Yellow-brown with greyish streaks; structure as in B_1.
D 44–48 in.	White band of marly (calcareous) material, very strong effervescence (not sampled).
C 50–62 in.	Pale yellow-grey; massive, easily crushed to loose condition; slight effervescence.

TABLE 10

Partial Analysis of Profile F11

Horizon	*Sand* %	*Silt* %	*Clay* %	*Fine clay* %	*Int. silt* %	pH	N %	O.C. %
A_0	..	..	..	..	..	6·5	1·55	21·85
A_2	82·1	11·1	6·8	4·0	5·4	6·4	0·03	0·30
A–B	87·1	7·0	5·9	1·7	3·8	6·4	0·01	0·14
B_1	88·5	2·4	9·0	5·2	0·4	6·2	0·02	0·02
B_2	83·6	4·7	11·7	7·1	2·4	6·0	0·01	0·11
C	84·3	5·5	10·2	6·0	3·8	7·5	0·01	0·03

Profile F11 represents a type of podzolic profile occurring on the finer-textured sandy deposits. This profile differs from the upland grey podzolic and brownish-grey podzolic types in possessing very thick A and A–B horizons, little or no textural differentiation, and only very slight accumulation of fine clay in the B. The moderate acidity of this profile might be ascribed to the calcareous parent material, but grey podzolic profiles of heavy texture, which also occur on calcareous deposits, are often considerably more acid in reaction. Because of these differences, profiles such as F11 have been described in Saskatchewan as a separate variety of podzolic soil within the grey wooded group.

Profile F5

Podzol-like soil on non-calcareous glacial outwash (mapped with Bodmin Association). Site—Meadow Lake Forest Reserve, about 53° 43′ N. Lat., 108° 22′ W. Long. Nearly level outwash plain. Well-drained surface, 0·5 per cent. slope to north-east. Wet lower subsoils with water table at 3 ft. Elevation 2,290 ft. Vegetation—poor jack-pine, low shrubs, and reindeer moss.

A_0 1–0 in.	Chiefly undecomposed needles and leaves (L).
A_2 0–3 in.	Light grey with faint pinkish tinge; small nutty-platy aggregates to loose, structureless; coarse sand.
B_1 3–8 in.	Light yellow-brown to yellow; loose, structureless, slightly heavier-textured than A_2—loamy sand.
$B_{2.1}$ 8–14 in.	Brownish-yellow, loose, structureless, gravelly sand.
$B_{2.2}$ 14–20 in.	Light brownish-yellow, otherwise similar to $B_{2.1}$.
C 20–32 in.	Light yellow-brown to very pale brown; wet, structureless gravelly sand.

TABLE 11

Partial Analysis of Profile F5

Horizon	*Sand* %	*Silt* %	*Clay* %	pH	N %
A_0	..	..	..	5·6	0·75
A_2	87·8	9·9	2·3	4·6	0·02
B_1	78·8	13·6	7·6	5·2	0·01
$B_{2.1}$	95·8	2·0	2·3	5·4	0·00
$B_{2.2}$	96·8	1·2	2·0	5·4	0·00
C	98·8	0·5	0·7	5·4	0·00

Profile F5 represents a podzol-like soil developed on coarse-textured acid parent material. With its thin, strongly acid, faintly pinkish A_2 and structureless B horizons, this soil bears considerable resemblance to the acid podzols of more humid regions. However, there is no evidence of any accumulation of nitrogen in the B_1, and a preliminary fusion analysis indicates that the B_1 contains only 0·3 per cent. more Fe_2O_3 than the A_2 horizon. This is a much smaller difference than is found in the podzolic soils developed on calcareous parent materials.

Preliminary studies of other acid podzolic soils of Saskatchewan have also suggested that humus does not accumulate in the B horizons of these soils. More complete analyses are required before the differences between calcareous and acid podzolic soils can be properly evaluated. Up to the present Saskatchewan workers have regarded these differences

as being due to the different nature of the parent materials, rather than to a different kind of soil formation. It should be noted that profiles similar to F4, developed on calcareous materials, may occur in close geographical association with profiles similar to F5, developed on non-calcareous materials. There is therefore no major climatic difference to account for the differentiating characteristics of these two types of podzolic soils.

Profile F9

Degraded black profile on calcareous boulder clay (Whitewood Association). Site—Near Kessock, about 51° 12′ N. Lat., 102° 2′ W. Long. Gently undulating ground moraine. Well drained 2 per cent. slope to east. Elevation 1,750 ft. Vegetation—recently cut-over aspen forest.

A_0 2–0 in.	Raw and decomposed organic matter (L, H).
A_1 0–4 in.	Dark grey to medium grey; cloddy-platy structure.
A_2 4–8 in.	Very pale brown; platy structure.
A–B 8–10 in.	Grey-brown transitional horizon, irregular cloddy structure (not sampled).
B_1 10–17 in.	Brown to yellow-brown; weak columnar structure, breaking to cubic and angular-fragmental aggregates.
B–C 18–23 in.	Yellow-brown to brownish-grey; cloddy structured, breaking to granular aggregates. Slight to moderate effervescence.
C 25–38 in.	Light yellow-brown, with grey streaks of $CaCO_3$, and small rusty spots. Massive, easily crushed to granular aggregates. Moderate to strong effervescence.

TABLE 12

Partial Analysis of Profile F9

Horizon	*Sand* %	*Silt* %	*Clay* %	*Fine clay* %	*Int. silt* %	pH	N %	O.C. %
A_0	..	..	..	..	..	6·3	1·40	16·02
A_1	54·6	28·8	16·3	10·2	17·3	6·2	0·28	3·38
A_2	61·0	27·2	12·2	5·9	17·6	6·4	0·06	0·76
B_1	50·8	21·6	27·7	19·2	12·1	6·4	0·05	0·57
B–C	45·0	26·7	28·3	15·8	17·2	7·6	0·04	0·42
C	46·8	25·4	27·7	15·1	18·0	7·7	0·03	0·23

Profile F9 is included in order to show the development of grey wooded (podzolic) leaching upon a black (chernozemic) soil. The relatively thick A_1 and the columnar structures of the B represent part of the former black columnar profile; the A_0 and A_2 horizons represent the podzolic development due to the invasion of forest vegetation on the original grassland prairie. The A_1 horizon is lighter in colour than the A_1 of a black soil.

The analyses shown in Table 12 confirm the evidence given by the morphology of profile F9. The chernozemic nature of the soil is shown by the relatively high content of nitrogen and organic carbon in the A_1 horizon. The podzolic nature of the soil is indicated by the acid reaction of the A and B horizons and by the accumulation of fine clay in the B_1. Compared with the grey wooded soils discussed above, profile F9 is

only slightly leached. It appears, however, that the process which produced the grey wooded profile is also operating on the degraded black soil.

Summary of Other Analyses

The inorganic carbon content of the non-calcareous mineral horizons of the various profiles is negligible, ranging from 0·0 to 0·09 per cent., with values of 0·1 to 0·2 per cent. in the A_0 horizons. In calcareous horizons, inorganic carbon ranges from 0·65 to 2·50 per cent. The soluble salt content, as indicated by conductivity measurements on the saturated soil extract, is negligible in all profiles except the podzolic-solonetzic (F12). The saline conditions in this profile have already been discussed.

Studies of other grey wooded soils of Saskatchewan provide information on exchangeable bases, clay minerals, and the A_{00} and A_0 horizons or forest floors. Base exchange studies by Riecken (1934) and Janzen (1941) indicate that calcium is the dominant exchangeable cation in grey wooded soils. This is confirmed by more recent studies (U.S.D.A. 1952).

Studies of the clay fractions of Saskatchewan soils, including a grey wooded profile, suggest that illite and montmorillonite-beidellite are the dominant clay minerals (Warder and Dion, 1952). Brown (1953) found montmorillonoids, a 14Å mineral, hydrous mica, kaolin, and calcite in the clay fractions of grey wooded soils from Alberta and Saskatchewan. He also reported evidence to suggest that recrystallization of the clay material is taking place in these soils.

Gross (1946) studied the forest floors in Saskatchewan and concluded that the organic surface horizons belong to the mor group. He recognized granular mor under spruce, 'dry' mor under jack-pine, and matted mor under deciduous forest.

With the exception of profiles F4 and F8, the present studies are limited to preliminary analyses of various types of Saskatchewan podzolic soils. Additional information on the chemical composition of the upland grey podzolic (grey wooded) profiles is given in Table 13, which gives the median values of chemical constituents found in ten profiles occurring on calcareous sandy clay loam to clay loam parent materials. Such profiles represent the dominant upland podzolic soils of the forest areas so far studied in Saskatchewan.

Referring to Table 13, it will be noted that the median values indicate a relatively high content of SiO_2 in the A_2 horizons, and a definite accumulation of Fe_2O_3 and Al_2O_3 in the B horizons. The A and B horizons are acid in reaction, with the lowest pH values occurring in the B. There is also an accumulation of nitrogen in the B. It should also be stated that all the profiles represented in Table 13 showed accumulation of clay in the B horizons and a relatively high content of silt in the A_2 horizons. The results below are in accord with the generalized statement on the composition of grey wooded soils made in the first section of this paper. They are also essentially similar to analyses reported from Alberta (Odynsky and Newton, 1950; Odynsky *et al.*, 1952).

TABLE 13

Median Values and Range in Values of Chemical Analyses of Ten Grey Wooded (Podzolic) Soils of Saskatchewan

(*Developed on medium-textured, calcareous, glacial deposits*)

Horizon	pH*	N* %	SiO_2 %	R_2O_3 %	Fe_2O_3 %	Al_2O_3 %
			Median Values			
A_2 . .	6·4	0·03	82·2	12·0	2·23	9·17
B . .	5·8	0·05	74·5	16·5	4·15	12·49
C . .	8·0	0·02	67·2	12·7	3·23	9·57
			Range in Values			
A_2 . .	5·4–6·9	0·01–0·07	77–85	8·6–13·5	1·8–3·0	7·4–10·5
B . .	5·0–6·9	0·02–0·08	68–79	14·3–17·6	3·3–5·7	10·7–13·3
C . .	7·5–8·1	0·01–0·04	55–77	11·1–14·3	2·6–4·0	8·6–11·0

* Values for pH and N calculated on analyses of seventeen profiles.

Problems of Classification and Nomenclature

Classification. In a previous paper (Moss, 1954) it was suggested that more knowledge of world soils is required before a satisfactory system of classification can be established. With respect to Saskatchewan, it was suggested that representative genetic profiles should be studied so that workers in other regions might secure a clear picture of Saskatchewan soils, and thus be able to compare them with other world types. Following these suggestions, the present study is an attempt to define the characteristics of Saskatchewan varieties of grey wooded (podzolic) soils. While more detailed chemical analyses of certain profile types are necessary to complete the picture, the studies already presented or referred to are sufficient for a preliminary discussion of these soils as a world group.

On the basis of morphology alone it is extremely difficult to separate the grey wooded soils from the podzols, in which a raw humus A_0, a well-developed, bleached A_2, and a brownish B were originally regarded as essential features (Glinka, 1927). In more recent years less attention has been paid to morphology, in some instances to the extent that podzol soils appear to be defined solely on the basis of chemical composition. While grey wooded soils are not identical to the podzols in chemical composition, they are reasonably similar, in content and relative accumulation of SiO_2, Fe_2O_3, and Al_2O_3, to some of the podzol soils reported by Glinka (1927) and De Sigmond (1938).

The grey wooded soils differ from the podzols in exhibiting a higher range in pH values and a correspondingly higher base status. They show less accumulation of organic matter and greater accumulation of clay in the B horizons. They also exhibit greater structural development. It should be noted that these grey wooded characteristics refer to medium-textured profiles developed on calcareous parent materials. These are the soils represented by profile F4 and by the analyses

shown in Table 13. Thus it may be suggested that the characteristics of clay accumulation, soil structure, and high base status referred to above are related to the kind of parent material. The morphological and chemical features of profiles F11 and F5 show the influence of lighter-textured, less calcareous to acid parent materials on soil formation in this region. It would seem, therefore, that the predominant grey wooded profiles (Table 13) are a product of calcareous, medium-textured parent materials and regional climatic-vegetational factors.

However, according to prevailing concepts of classification it is necessary to place the grey wooded soils with the so-called podzolic group. As in the comparison made with the podzols, the grey wooded soils show some similarities and some differences when compared with podzolic soils. Among the latter types, the grey-brown podzolic appears to show the greatest similarity to the grey wooded. The two soils are essentially similar in composition, notably with respect to content and distribution of SiO_2, Fe_2O_3, and clay. They differ chiefly in morphology —the grey-brown podzolic possessing little or no A_0 horizon, a well-developed crumb-structured A_1, and a greyish-brown to yellow-brown A_2. Descriptions and analyses of American grey-brown podzolic profiles have been reported by Marbut (1935). Stobbe (1952) and Nygard *et al.* (1952) have discussed the comparative morphology of the grey-brown podzolic and grey wooded soils.

According to Thorp and Smith (1949) grey wooded soils appear to be correlatives of the grey forest soils of Russia. Williams and Bowser (1952) state that some American grey wooded soils have many characteristics in common with the grey forest soils described by Stebutt. Muir* regards the grey wooded soils as essentially similar to the grey forest. Undoubtedly these soils may be grouped together as podzolic soils, but there does not appear to be any record of their exact degree of similarity. In fact, literature available in English suggests there are important differences between these two groups of soils.

Reviewing Glinka (1927) and Joffe (1949), it appears that all grey forest soils possess A_1 horizons, varying in colour from grey to dark brown, and characterized by a so-called 'pea' structure. The A_2 horizon is grey and brownish-grey in colour and has a characteristic nutty structure—so characteristic of these soils that Dokuchaev is reported to have named them 'nutty soils'. Both A horizons are relatively high in organic matter. The B horizons are brown in colour and possess large nutty structures above and prismatic structures below. Chemical analyses indicate that the grey forest soils contain more humus than the grey wooded soils and, except in the light grey varieties, show less accumulation of Fe_2O_3 and Al_2O_3. Mechanical analyses indicate clay accumulation in the B horizon—a characteristic shared by the grey wooded soil. If the above-mentioned features are typical, they suggest that grey forest soiis differ considerably from the grey wooded soils of Saskatchewan.

Hallsworth *et al.* (1953) have discussed Australian soils with podzol-like morphology, including podzol, solod, and solonetz profiles. These

* Private communication.

authors state that inspection of the literature suggests that the grey wooded soils of Canada belong to the solodic group. The latter group is characterized by bleached A_2 and heavier-textured B horizons, and as stated by the authors: '. . . analyses of these soils show that, in contrast to the podzols, the exchangeable bases of the deeper subsoils are always dominated by (sodium+magnesium)'. It will be obvious from this statement that the grey wooded soils of Canada do not belong to the solodic group. The only profile which might qualify as the above solodic soil is the podzolic-solonetzic, but this is already recognized in Canada as a complex profile showing the effect of podzolization upon a former solonetzic or solodized soil. With this possible exception, the grey wooded soils, as already stated, are dominated by exchangeable calcium. On the basis of the Australian classification, the grey wooded soils of Canada would appear to belong to the 'sidero-pelo-lepto podzols' (Ibid.).

Nomenclature. To complete the present discussion, further reference should be made to the nomenclature of grey wooded soils. As already stated, Saskatchewan workers prefer the name 'grey podzolic' (or 'grey-podzol') because they desire to indicate that these soils belong to the podzol group. The name 'grey wooded' is meaningless in itself, particularly to anyone not familiar with these soils. A similar difficulty has existed with respect to the prairie soils of the United States and the grey forest soils of Russia. Unfortunately, American workers have recently used the term 'grey podzolic' to describe still another type of podzolic soil. In order to avoid confusion it would seem that the grey wooded soils might be identified by the rather clumsy designation of 'grey wooded podzolic'. This, however, is no more cumbersome than the terms 'grey-brown podzolic' and 'red-yellow podzolic'.

Another suggestion is that the grey wooded soils should be recognized as podzol soils of high base status, and that a name should be adopted which would identify this characteristic. In any event, it seems logical to suggest that, so long as the terms 'podzolic' and 'podzol' continue in general use, all soils regarded as belonging to either of these types should be so designated.

Finally, there is the problem of naming the individual genetic profiles which make up the podzolic soils found in Saskatchewan and other parts of western Canada. It will be evident that the profiles discussed in this paper cannot be fully identified by simply calling them 'grey wooded'; terms such as 'upland grey podzolic', 'brownish-grey podzolic', 'podzolic sand', 'depression podzolic', and 'podzolic-solonetzic' are required to cover the ranges in profile development in the forest soils of this region. If it is argued that all of these profiles belong to the group now known as grey wooded soils, it must likewise be recognized that there is more than one kind of grey wooded profile.

Summary

This paper constitutes a review of the major studies carried out on the grey wooded (podzolic) soils of western Canada and also presents some recent work from Saskatchewan.

The morphological and chemical studies confirm earlier conclusions

(Moss, 1937) that the podzolic soils of Saskatchewan form a distinct branch of the podzol family.

A number of varieties or types of these soils have been recognized, and further analytical work is required on some of these profiles before their distinctive characteristics can be clearly defined. The problems of classifying and naming these soils as a world group have been discussed briefly. It is suggested that the words 'podzolic' or 'podzol' should be included in the recognized descriptive name of these soils.

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The authors acknowledge the assistance of the following members of the Saskatchewan Soil Survey: W. K. Janzen in sampling, and J. G. Ellis and A. K. Ballantyne in laboratory work. Acknowledgement is also made to Professor J. Mitchell, University of Saskatchewan, for his valuable criticicm of the manuscript.

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1. Grey wooded soil similar to profile F4. Forest cover destroyed by fires

2. Newly broken land, showing complex of black (chernozemic) and depression podzolic soils. Near profile F8

H. C. MOSS AND R. J. ST. ARNAUD—PLATE I

3. Burnt-over jack-pine forest, showing second growth. Pine forest is associated with profile F5 and other non-calcareous podzolic soils

4. Cultivated grey wooded (podzolic) soil, exposing thick, light grey A_2 horizon

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SOIL MINERALS OF THE GOLD COAST

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ALL soils undergo a series of changes. Initially they consist of freshly accumulated fine- and coarse-grained rock material and minerals. This is followed by a stage in which they are chiefly made up of more or less rounded, hard, and very resistant minerals. The last stage is when the soil only contains the products of alteration and decomposition. Mineralogical investigation of the soil, therefore, reveals a great deal about the soil's age (weathering stage), classification, fertility, origin, and transport. It is frequently difficult to identify minerals in detrital soils, however, as they are masked by alteration products adhering to them.

It is necessary, therefore, first to remove these coatings or films. This can be done in many ways. In view of the fact that the equipment available was rather limited, this was done simply by soaking with 7 per cent. (2 N) HCl (1:5) for a period of 3 days, without heating. Approximately 25 g. soil were soaked in 100 ml. dilute HCl. When this 3-day period had elapsed, the soil was washed thoroughly with rainwater; this eliminated all dirt and left only the minerals. These are then concentrated, dried in the sun, and passed through a 100-mesh (0·15-mm.) metal-gauze sieve. They were then mounted on a glass slide with the aid of Canada Balsam. The coarser fractions were only studied with a hand magnifying glass or a binocular microscope. Usually, they consisted solely of rock fragments, concretions, quartz, and opaque minerals, though sometimes they also contained pyroboles (= pyroxenes+amphiboles), garnet, epidote, rutile, and mica flakes. The fine-grained fraction, which had been mounted, was counted under a polarizing microscope. Counting is a necessary procedure, if one wishes to form an approximate idea of the mineral composition of the soil, coupled with the advantage of avoiding an over-estimation of the coloured and opaque minerals. On each occasion, one hundred grains along an arbitrary straight line were counted through the slide.

It was impossible to separate the heavy fraction, as no bromoform was available.

Six groups of dark-coloured soils from the dry savannah plains, east of Accra, were selected for this investigation. Groups 1 to 5 represent the melanites or alkaline, black, heavy clays, derived from a basic hornblende gneiss (garnetiferous), while Group 6 includes the alluvial fluvio-marine soils (alluvites).

In addition, two different groups of bright-coloured soils (rubrites), from the forested hills of Ashanti, were selected. Group I includes the drifted mantle soils, covering *in-situ* soils, and Group II purely residual soils. These residual soils are derived from schists (Bekwai series), mica granites (Kumasi series), or from mica gneisses (Swedru series).

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The groups were as follows:

Group 1: Three distinct profiles to enable the approximate mineral composition of the parent material of the black clays to be determined. They were all shallow, stony, hill soils (except the Bumbi), with an acid pH of 6–6·6, and were of a light texture.

Group 2: One buried profile, which was not given further consideration.

Group 3: Taken from four pits in the centre of the black clay area, characterized by dark-coloured, heavy clays, with an alkaline pH of between 7·8 and 8·2.

Group 4: Taken from three pits near the boundary of this area, where there were also dark-coloured, heavy clays, though with a pH varying between 6·6 and 7·6.

Group 5: Taken from four pits outside the area for the purposes of comparison. They are all black, *acidic* clays with a pH of 6 to 6·8.

Group 6: Derived from six pits near the mouth of the River Volta. They are alluvial soils, the texture and pH of which exhibit considerable variation.

Group I: Five profiles of a very acid, but less heavy, red loam, with a pH of 5 to 5·8.

Group II: Six profiles of a less acid, but very heavy, red loam, with a pH of 5·4 to 6·8.

Tables 1 and 2 and the pit maps show that there is only a small mineralogical variation in these profiles, in spite of the differences in colour, pH, or texture of the layers selected for these experiments. This should occasion no amazement, as these properties are independent of these relatively coarse-grained minerals, being governed by the ultramicroscopic part of the soil.

In the field, the melanites generally show residual profiles, in which the gradual transition from parent rock to soil is evident. Sometimes, however, one also encounters transported profiles together with stonelines. A rather elaborate mineralogical analysis was necessary, therefore, in order to solve this problem. These countings led to the following results: the composition of the more important parent materials of the black clays appears to be (in Group 1) rutiliferous epidote amphibolite, garnetiferous pyroxenite, and *garnetiferous hornblende gneiss*. They are characterized by almost equal parts of quartz, pyroboles, and garnet. The Bumbi, moreover, contains a great deal of epidote and rutile. In addition to the many pyroboles, the presence of a small quantity of plagioclase, together with the angular form of the minerals, proves that all these soils are young or juvenile, and have almost not been transported.

The soils encountered in the centre of the black-clay area (Group 3) indicate clearly that they are of garnetiferous hornblende gneiss origin. They contain chiefly quartz and garnet. A small amount of hornblende is still in evidence, while traces of plagioclase also occur, which demonstrates conclusively that these soils have not been weathered out, but are still virile. The fact that the heavy garnet is more concentrated than the lighter quartz indicates that these soils are not perfectly *in situ*, but that they have been subjected to a small amount of centrifugal transportation and sortation. That transportation has occurred is also inferred from the grains, some of which are sub-rounded. The isolated peaks can only partially be centres of origin. This is probably not so, however, for numbers 7 and 8.

There is a great decrease in the quantity of garnet encountered near the boundary of the same area (Group 4), together with a large increase

TABLE I

Minerals of the Accra Plains

Pit no. (map A)	Soil series	Colour and texture	Depth (in.)	pH	Quartz	Plagioclase	Augite	Epidote	Garnet	Hornblende	Kyanite (Disthene)	Pyroboles (Fibrous)	Rutile	Staurolite	Tourmaline	Zircon	Opaque	Diverse
				Group 1 (Parent materials of the melanites)														
1	Bumbi	dBc	6–14	6·0	18	..	+	25	12	34	..	..	8	..	..	..	3	..
	,,	dBc	14–18	6·2	15	..	1	19	10	39	..	..	10	..	..	1	5	..
2	Kloyo	dBl	1–8	6·0	33	1	..	2	27	25	..	..	5	..	..	1	6	..
	,,	dBl	>8	6·0	37	1	..	1	29	23	..	..	3	..	..	2	4	..
3	Osudoku	dBc	0–7	6·6	25	1	1	3	15	32	..	13	3	..	..	1	6	..
	,,	dGc	>7	7·0	21	1	2	5	17	34	..	14	1	..	..	+	5	..
				Group 2 (Buried soil—Jongwa)														
4	Jongwa	dBc	5–15	6·4	27	1	..	..	45	11	..	+	2	..	..	+	14	..
	,,	Bs	60–70	7·2	22	1	..	..	50	9	..	+	+	..	..	1	17	1Hy
	,,	dBc	101–19	7·8	25	+	..	..	51	9	..	1	1	..	..	+	13	..
				Group 3 (Central melanites)														
5	Tachem	Bc	41–58	7·8	22	?	..	..	69	3	..	..	3	..	..	+	3	..
	,,	dBc	58–69	7·9	25	..	..	..	63	2	..	..	5	..	..	2	3	..
6	Akuse	dBc	41–54	8·0	35	+	..	4	47	3	..	..	6	..	..	1	4	..
	,,	pBc	54–66	8·2	31	..	..	3	52	2	..	..	5	..	..	2	5	..
7	Prampram	dBc	15–26	7·8	21	..	..	1	70	1	..	..	3	..	+	1	3	..
	,,	pBc	26–38	8·0	26	?	..	+	64	2	..	..	5	..	..	+	3	..
8	Akuse	Gc	0–24	7·8	37	..	..	+	53	1	..	..	3	..	..	+	6	..
				Group 4 (Marginal melanites)														
9	Akuse (Brown)	YBc	39–57	7·6	81	..	..	3	5	2	..	..	2	..	..	2	5	..
	,,	YBc	57–65	7·8	83	..	..	2	4	1	..	..	3	..	+	2	5	1Si
10	Jaw Wulu	Gc	26–38	6·6	77	..	..	7	3	+	..	..	5	..	..	2	6	..
	,,	Gc	38–54	7·0	79	..	..	6	2	1	..	..	6	..	..	1	5	..
11	Akuse over Krabo	dGc	10–35	6·6	80	..	..	4	5	2	..	..	3	..	..	1	5	..
		Bs	88–114	7·0	81	..	..	7	3	1	..	..	2	..	..	2	4	..
				Group 5 ('Outside' melanites)														
12	Osibi	Bc	25–39	6·0	86	..	..	3	3	..	..	..	2	..	..	1	5	..
	,,	Gc	39–48	6·0	85	..	..	2	2	..	..	..	5	..	..	2	4	..
13	Tachem	dBc	9–30	6·2	89	..	..	3	1	..	..	..	2	..	..	+	5	..
14	Jaw Wulu	Gc	8–16	6·0	92	..	..	3	1	+	..	..	..	..	..	1	3	..
15	Akuse	Gc	10–29	6·8	89	..	..	+	5	..	..	..	+	+	..	2	4	1Sp
				Group 6 (Alluvites)														
16	Kakum between Chichi-were	Bc	20–39	6·0	91	..	..	+	+	5	..	..	+	..	..	1	3	..
		pBs	39–48	6·5	87	..	..	3	3	2	..	..	+	+	+	..	5	1Hy
17	Densu	Bc	16–32	5·0	85	..	..	2	2	+	..	..	..	..	..	..	11	..
18	Ayensu	Gc	10–22	6·0	90	..	..	2	..	..	..	..	1	..	..	2	5	..
19	Oyibi	dGc	8–19	7·0	73	..	..	3	2	+	..	..	..	+	+	2	20	..
20	Keta	dBs	5–18	7·0	91	..	..	+	..	..	..	..	1	+	+	1	7	?
21	Muni	Bc	6–18	8·0	71	..	..	4	18	..	..	..	+	+	..	2	5	..

Abbreviations on Table II

TABLE 2

Minerals of the Upper Tano Basin

Pit. no. (map B)	Soil series	Colour and texture	Depth (in.)	pH	Quartz	Plagioclase	Augite	Epidote	Garnet	Hornblende	Kyanite (Disthene)	Pyroboles (Fibrous)	Rutile	Staurolite	Tourmaline	Zircon	Opaque	Diverse
	Group 1 (Drifted mantle soils)																	
1	Chira over Kumasi	Ol	24–45(dr)	va	77	..	..	1	..	..	2	..	..	..	+	2	18	..
	,, ,,	Ol	45–73(r)	va	68	..	..	1	..	..	..	..	+	..	..	+	31	?
2	Chira over Kumasi	Oc	24–39(dr)	5·0	71	..	..	+	..	..	1	..	..	..	1	+	27	..
	,, ,,	Rc	39–44(r)	va	54	..	..	..	+	..	+	..	..	..	..	1	45	..
3	Chira over Bekwai	Rl	14–24(dr)	5·4	76	..	..	+	..	..	3	..	..	+	+	..	21	..
	,, ,,	Rl	43–57(dr)	5·6	76	..	..	+	..	..	5	..	+	?	..	..	19	..
	,, ,,	Rl	57–79(r)	5·6	68	..	..	1	..	..	6	..	+	..	..	..	25	..
4	Akumadan	dRl	29–73(dr)	5·8	80	..	..	?	..	..	1	..	..	..	..	..	19	..
	,,	pRc	113–32(r)	va	77	..	..	+	..	..	..	..	..	..	..	..	23	..
5	Chira	Oc	15–25(dr)	6·4	84	..	..	..	+	..	..	..	..	..	..	..	16	..
	,,	Ol	72–84(r)	5·5	79	..	..	?	..	..	..	..	..	..	..	?	21	..
	Group 2 (Residual soils)																	
6	Kumasi	Rl	60–77	6·2	53	..	..	1	..	+	?	..	..	..	..	+	46	..
7	Bekwai	Rc	45–66	6·8	75	..	..	1	..	..	..	..	..	+	+	..	24	..
8	,,	Rl	16–25	6·0	55	..	..	+	..	..	?	..	..	..	..	..	45	..
	,,	Rl	51–72	5·4	51	..	..	..	..	..	..	..	+	..	..	..	49	..
9	,,	pRBl	102–29	5·2	78	..	..	+	..	..	..	..	..	..	+	..	22	..
10	,,	Rl	36–62	5·4	83	..	..	?	..	..	..	..	..	..	..	..	17	..
11	Swedru	Ol	56–72	6·5	90	..	..	..	..	1	..	..	..	..	1	?	8	..

p—pale
d—dark

B—brown
O—orange
G—grey
Y—Yellow
R—red

c—clay
l—loam
s—sand

dr—drifted
r—residual
va—very acid
+—present

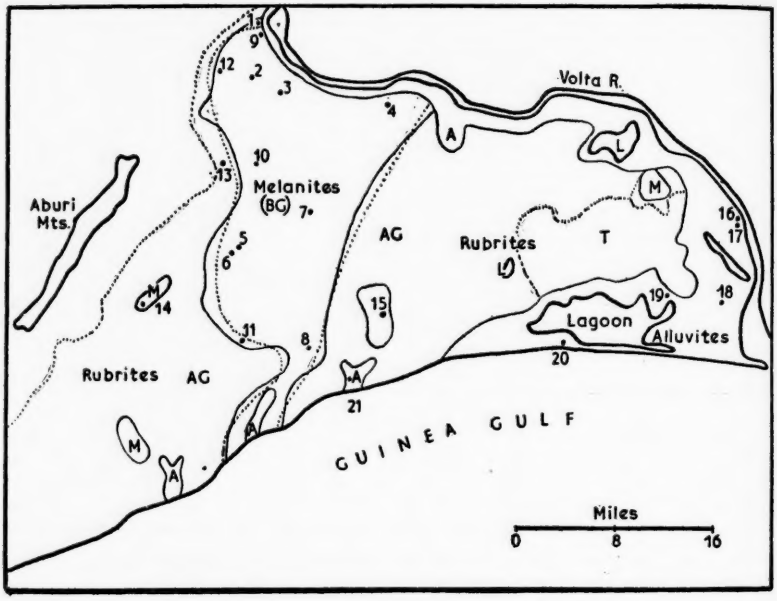
Hy—Hypersthene
Si—Sillimanite
Sp—Spinel

in quartz. This fully bears out the 'centrifugal transportation' of material, mentioned above. The fact that there must be some hornblendic rock in the vicinity is apparent from the fact that a few hornblende grains were counted. These soils vary between senile and virile and have also been transported a little.

Turning to the soils outside this area (Group 5), the quartz content has increased enormously, and this mineral predominates strongly. All the other minerals are present, but only in very limited quantities. These soils are very definitely senile. Another significant fact is that the minerals in these soils are much more rounded than those in the other groups. This was particularly clear in the coarse-grained fractions, indicating slightly more transport.

Finally, the minerals of the alluvial soils (Group 6), which have only been included for purposes of comparison. It is not surprising that they consist chiefly of quartz. The remainder of their content is made up

of many other minerals, although they are only present in small quantities. Moreover the minerals are rather rounded, especially the coarser ones. A varying mineralogical composition of this kind is not unusual in alluvial soils, where the make-up normally varies considerably. Likewise, alluvites invariably exhibit a greater degree of transportation and



PIT MAP A.

SCALE: 1/500,000

..... Boundary of the Rocks:
AG–acidic gneiss,
BG–basic gneiss,
T–tertiary deposits.

——— Boundary of the Soils:
A–alluvites (7 series over Quaternary deposits).
M–melanites (9 series over basic gneiss).
R–rubrites (18 series over acidic gneiss and tertiary deposits).

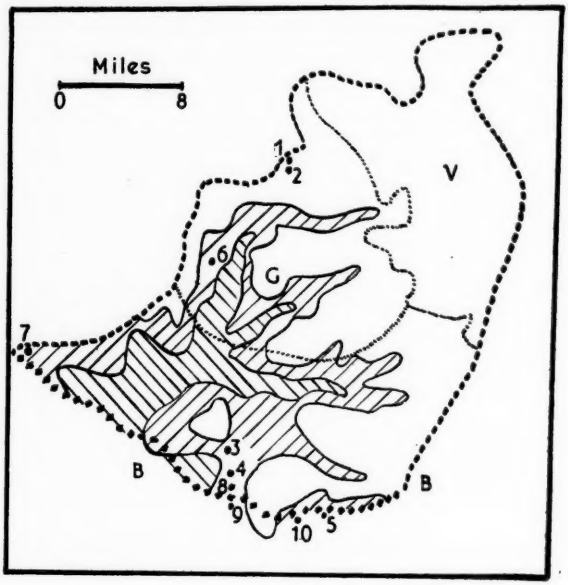
L–Lagoon.
.21 Pits.

sortation. Sample No. 21 is rich in garnet, because it was found near the garnetiferous hornblende gneiss of its hinterland. The large percentage of opaque minerals in Sample No. 19, however, is rather remarkable.

As far as the clay minerals $<2\mu$ are concerned, the black-clay properties led one to assume in advance that they were chiefly montmorillonitic. An X-ray ($Cu_{K\alpha}$) diagram of a heavy black Akuse clay (after treatment with 10 per cent. hydrogen peroxide and dilute (0·2 N) hydrochloric acid) exhibited the typical montmorillonitic characteristics, in addition to traces of kaolin and quartz. A trace of calcite was also to

be expected. An X-ray photograph showed all the usual characteristic lines. This tallies completely with the results obtained by Stephen (1953) who also found the same minerals in similar soils.

The following results were obtained in respect of the Ashanti soils, collected in the Upper Tano Basin. The chief problem with these Tano



PIT MAP B.

SCALE: 1/500,000.

----- Boundary of the River Basin.

..... Boundary of the Rocks:
V–sandstones,
G–granites,
B–phillytes and schists.

——— Boundary of the soils (3 kinds).

♦♦♦♦ Road (motorable).

Mantle soils (16 series in upland positions),
Mixed soils (transition zone),
Residual soils (12 series in lowland positions),
} Rubrites.

.10 Pits

soils was to distinguish the drifted mantle soils from the residual soils. The differences are generally obvious, although the surveyor in the field is not always so fortunate, for there are many problems, especially in the transition zone with mixed soils. Most of the samples, therefore, were collected in this area. Some of the attendant difficulties can be overcome with the aid of a trained eye and experienced touch, but even so there are many cases in which finding a satisfactory explanation is a tricky proposition. This, however, is where microscopical examination can help.

The general mineralogical impression got from all these soils is that they are senile, lateritic soils. This means that there are only a few weatherable minerals remaining. Practically no pyroboles or plagioclases are encountered, and the bulk of the minerals consists of resistant types, like quartz and opaque ores (magnetite, ilmenite, &c.). Soils found in pits 6, 8, and 11 were particularly rich in these hard components. In addition, they also differ from the melanites, apart from their colour, texture, and pH, in having minerals like kyanite, staurolite, and tourmaline, which are encountered more frequently in the rocks of this area.

If we compare the drifted with the residual layers (in Group I), we are struck by the fact that the drifted horizons contain more quartz and less opaque ores. The residual horizons, on the other hand, contain less quartz and more heavy ores. This is readily understandable, as sortation invariably occurs at the same time as transportation. In other words, the heavy minerals are left behind and the lighter ones carried along. Reasoning along these lines, it will be obvious that the quartz is more concentrated in the moving layers, while the heavier minerals remain in the more stable part of the soil. Still more significant in the case of the drifted layers, however, are the perfectly rounded quartz grains, resembling small, colourless shot. These are especially noticeable in the coarse fractions. Only subangular quartz was found in the same fraction of the residual layers—and in all the other residual soils of Group II as well. Apart from the general remarks which have been made already, this group (II) does not exhibit any other aspects worthy of specific mention.

For the purposes of comparison, a sample from the Ayensu Basin has been included. It is a Swedu series, which outwardly shows a strong resemblance to the Kumasi series. Visually, they are very difficult to distinguish from one another, and apparently mineralogically as well.

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THE REACTION BETWEEN BENTONITE AND CERTAIN NATURALLY-OCCURRING COMPOUNDS

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NUTMAN (1951) studying the effect of adsorbents on the process of nodulation in clover plants (*Trifolium pratense* L.) noted the formation of coloured complexes on the surface of the bentonite when this mineral was added to the rooting medium. Later Nutman (1952) claimed that in the presence of bentonite a stimulation in nodule numbers occurred on inoculated clover plants through the adsorption of inhibitory compounds secreted by the roots.

As these root secretions may be related to the compounds giving rise to the colour reaction on the bentonite, an understanding of the mechanism involved in the latter reaction might be expected to help in the identification of these root secretions. The reaction between bentonite and certain naturally-occurring compounds has therefore been studied in some detail.

Bentonite is a montmorillonite mineral giving a characteristic X-ray diagram and having the general formula $4SiO_2A1_2O_3xH_2O$. In bentonite, some of the alumina in the crystal lattice is replaced by ferric oxide. Certain chemical compounds, e.g. diamines, are known to form coloured complexes after adsorption on to alumino-silicate clays (Weil Malherbe and Weiss, 1948; Hendricks and Alexander, 1940; Hauser and Leggett, 1940), and these workers suggested that an oxidation, possibly due to the iron present in the lattice, may be an important step in the reaction. Recently Kayser *et al.* (1952) have claimed that other types of reactions may occur on the bentonite surface.

In the present series of experiments, clover plants were grown on agar slopes in test-tubes as described by Thornton (1930). The adsorbents to be tested were added to the plants at the time of inoculation with *Rhizobium* strains.

Preliminary results confirmed the observation of Nutman that a colour reaction developed in the neighbourhood of the roots after the addition of bentonite. The colour first developed about 20 days after the germination of the seed and usually first occurred in the hypocotyl region and later in the neighbourhood of the lateral roots and occasionally near the nodules.

The nodule bacteria were not the cause of the reaction nor is it dependent on the process of nitrogen fixation since the colour is rapidly developed with uninoculated plants provided that inorganic nitrogen is supplied to the plant. The colour did not appear if the plants showed poor growth, nor did it appear with all the clover plants tested, even if growing healthily.

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The colour region extended outwards from the lateral and main roots and was typically blue in colour, although mauve and violet colours also appeared. These latter colours occupied a more diffuse zone than the more clearly defined blue zones. No colours developed when the bentonite was dispersed in the agar.

Owing to isomorphic replacement in the bentonite crystal lattice, the latter acquires an overall negative charge which may be compensated by the presence of exchangeable cations and it is possible to prepare calcium, sodium, and potassium bentonites. The effect of these bentonites on the colour formation and of other minerals allied to montmorillonite, viz. hectorite (in which magnesium replaces aluminium—and lithium is present as an essential constituent in the lattice), mica, and illite, are shown in Table 1.

TABLE 1

The Effect of Crystal Lattice on Colour Formation with Clover Plants

Adsorbent added	Colour formed on the adsorbent in the neighbourhood of the roots.
Commercial Wyoming bentonite	Blue.
Sodium bentonite	Blue.
Calcium bentonite	Blue.
Potassium bentonite	Blue, colour intensified over other bentonites.
Lithium bentonite*	Blue.
Hectorite	Blue.
Mica	No colour formation.
Illite	No colour formation.

* This sample was kindly supplied by the Pedology Department, Rothamsted.

All the treated bentonites gave the usual reaction with the plant root secretions whilst hectorite gave reduced colour formation. No colour developed on the mica-illite group of minerals; a result suggesting that the type of crystal lattice may be important for the formation of the colours.

In certain experiments bentonite was incorporated into the agar slopes, and chemical compounds known to produce colour reactions with bentonite were added. At low concentrations enhanced colour formation on the bentonite could be achieved by pretreating the agar either by washing with tap water or by the addition of charcoal. Agar may therefore contain small quantities of an inhibitor which may interfere with the colour development. Charcoal (1 per cent.) was therefore incorporated into the agar slopes on which the clover plants were grown, and this increased colour formation when bentonite or hectorite was subsequently added to the tubes.

However, the presence of agar is not essential for the colour reaction since the agar can be replaced by filter-paper slopes. Colour production also occurs, but in considerably reduced quantities, when the plants are grown in sand-bentonite mixtures or in water culture with bentonite in the bottom of the tube. The addition of agar extracts to the filter-paper slopes or to the water-culture experiments did not lead to increased colour production.

Cellobiose, glucose, and maltose in aqueous solution are not generally considered to form inter-lamellar complexes with montmorillonite. However, bentonite treated with these compounds reduced Fehling's solution and charring occurred if the bentonite was dry sterilized at high temperatures. The addition of the treated bentonite to the clover plants led to reduced colour formation. These results, reported in Table 2, suggested that adsorption of compounds on the crystal lattice is an important step in the formation of the colours. But since lithium-treated bentonite (which does not swell when placed in water) gave colour formation, expansion of the crystal lattice is not essential for the development of the colours.

TABLE 2

The Effect of Pretreatment of the Bentonite with Polyhydroxyl Compounds

(*Bentonite was suspended in the appropriate solution for several days; washed with water and dried at room temperature*)

Treatment	*Number of plants tested*	*Number showing colour formation*	*Colour produced*
Untreated bentonite . .	20	14	blue
Cellobiose treated . .	10	1	blue
Glucose treated . . .	20	5	blue
Maltose treated . . .	20	3	blue
Untreated bentonite plus 2% glucose to nutrient solution	18	16	blue

At various stages of growth, plants were removed from the tubes to which bentonite had been added; but in no case did any colour development occur after the plants had been removed. No appreciable delay occurs therefore between the secretion of the compounds and the subsequent colour development. The formation of the coloured compounds is not due to the presence of plant debris or to sloughed-off root cells since no colours develop when the leaves are removed from the plants and the roots left to decay. Water extracts of the roots were also made and added to bentonite but no colour formation occurred.

Selected lines of clover plants, which had been raised for other purposes, were tested for colour production. The results are given in Table 3 and indicate that there is a considerable variation in the amount of coloured material formed and in the number of plants exhibiting colour production. This variation may be related to genetical factors. Consequently selected plants were crossed and the seed tested for colour production. The results are given in Table 3 A and indicate that the secretion of the compounds leading to colour formation is not inherited on any simple genetical basis but that it may be possible to raise lines of clover plants to give increased yields of the coloured compounds which may be required for the chemical analysis.

TABLE 3

Survey of Clover Families for Colour Formation with Bentonite

Family	*Number of plants sown*	*Number of plants showing colour development in the neighbourhood of the roots*
1	15	6
2	20	4
3	22	14
4	20	6
5	20	9
6	19	3
7	20	10
8	20	10
9	20	7
10	12	0
11	20	5
12	20	6
13	20	13
14	19	5

To extend the scope of the observations, several other species of plants were grown in contact with bentonite. Results shown in Table 4 indicate that the secretion of compounds leading to the formation of the coloured compounds on the bentonite is not confined to leguminous plants.

TABLE 3 A

Effect of Crossing Colour-producing Plants with Plants showing no Colour Development

Family		*Number of plants of progeny tested*	*Number of plants showing colour formation*
1. 73×71	Both parent plants showed colour formation with bentonite.	17	4
2. 70×78		15	7
3. 76×75		17	5
1. 86×83	Both parent plants showed no colour development.	20	3
2. 87×85		20	1
3. 87×84		20	5

Chemical Tests on the Coloured Bentonite

The reacted bentonite from the clover experiments was separated from the remainder of the bentonite. On the addition of acid, the colour on the bentonite was intensified, whilst in alkaline solutions decolorization occurred. The effect was reversible.

The addition of organic solvents had no immediate effect on the colour, but on standing overnight the coloured compounds were eluted from the bentonite when 70 per cent. aqueous acetone or pyridine was used. Pure or acid acetone, ethyl and butyl alcohols did not affect the colour.

After treatment of the coloured bentonite with aqueous acetone the bentonite was centrifuged off. This bentonite gave the usual colour reactions with chemical compounds, indicating that the acetone treatment had no effect on the bentonite crystal lattice. Acetone was removed from the supernatant liquid at room temperature and also at 0° C. and the resulting aqueous solution retested with bentonite. No colour developed. The compounds did not appear to be removed with the acetone and it seems likely that the eluted compounds are unstable in aqueous solution. This hypothesis would be in agreement with the small amount of colour produced when the plants are grown in water culture. Alternatively the concentration of the compounds in the aqueous extracts may be too low for any colour formation to occur. A minimum concentration of 0·1 mg. per ml. of added β-indolyl acetic acid was required for the formation of colour on bentonite.

Addition of Chemical Compounds to Bentonite

Certain compounds when added to bentonite give rise to the formation of coloured compounds on the surface of the bentonite (Table 5).

TABLE 4

Survey of Plant Species giving the Formation of Coloured Complexes with Bentonite

Species tested	*Colour produced*	*Effect of acid and alkali on the colour*
Vicia hirsuta	orange	acid—decolorized, alkali—intensified
Lotus corniculatus . . .	black with green tinge	acid—prussian blue colour formed alkali—dull grey colour formed
Anthyllis vulneraria . . .	grey	acid—blue green colour formed, alkali—decolorized
Nicotiana tabacum . . .	faint yellow colour	acid—decolorized, alkali—no effect
Chrysanthemum cerinetum . .	faint pink	acid | alkali / possible faint decolorization
Hyoscyamus sp. . . .	pale yellow	acid—no effect, alkali—slight intensification
Linum sp.	intense yellow	acid—decolorized, alkali—intensification

Of the commonly occurring compounds tested, only tryptophane, dihydroxyphenylalanine, and β-indolyl acetic acid gave a positive reaction.

Consideration of Table 5 suggests that there may be a general parallelism between the colours developed by these compounds with bentonite and with ferric ions. This is strikingly shown by the colour reaction given by salicylic acid and indolyl derivatives. The results obtained are

therefore not inconsistent with the view that the iron present either in the bentonite crystal lattice or as an impurity may be involved in the formation of the coloured complexes on the bentonite surface. The effect of the type of crystal lattice on colour formation noted in Table 1 could then be explained by suggesting that as some montmorillonites are weathered products of the micas, migration of the lattice-held-iron would be more rapid in the degraded material.

Further support for this hypotheses regarding the importance of iron in the reaction was obtained using crude hectorite and p-phenylene diamine. Colour only developed on the hectorite after 2–4 hours whereas hectorite containing iron impurity gave an immediate reaction. In addition, the colour complex formed on bentonite with indolyl acetic acid can be eluted with 70 per cent. acetone. The supernatant is colourless and the colour can be re-formed on the bentonite by removal of the acetone, indicating that some component of the bentonite lattice is involved in the colour formation.

Bentonite was also treated with ferric alum. On the addition of potassium ferrocyanide a blue colour developed on the bentonite indicating that free ferric ions were present on the bentonite surface. This bentonite was washed and added to the clover plants, and of the nineteen plants tested all but one showed colour formation on the bentonite; a higher percentage than was usually encountered. However, whilst the intensity of the colours was not greater than in the untreated samples, in the iron-treated bentonite samples the coloured areas were more diffuse. A greater variation in colour was also produced and the pink-mauve colour became very pronounced. Whether this variation in colour is due to the presence of one or more compounds secreted by the plant is not known.

Comparison of the effects of reagents on the coloured bentonite obtained from the plant experiments and from added dihydroxyphenylalanine and indolyl acetic acid (Table 6) suggests that the colour reaction between bentonite and indolyl derivatives resembles closely the reaction between bentonite and the root secretion from the clover plants. Indeed the pink colour seen in the tubes may be due to these compounds. Various inorganic and organic compounds have been added to the indolyl acetic acid–bentonite system including extracts prepared from the clover roots, but so far it has not proved possible to reproduce the blue colour formed by the root secretions. Indolyl pyruvic acid produces a blue colour with bentonite and this compound has recently been reported to occur in maize plants (Stowe and Thimann, 1953).

Since tryptophane gives a colour reaction with bentonite, the liquid from the water culture experiments was concentrated and tested with ninhydrin for the presence of amino acids. The tests, however, were negative.

In conclusion, it may be stated that the colour reaction between bentonite and indolyl derivatives resembles that between bentonite and the root secretions from the clover plants. Further progress towards the identification of these secretions will depend on the methods for obtaining increased yields of the coloured material and for the recovery of the eluted material from the reacted bentonite.

TABLE 5

Colours produced by Various Chemical Compounds with Bentonite and with Ferric Chloride

Compound added	*Colour with bentonite*	*Colour with ferric chloride*
	in acid solution	
p-phenylene diamine	blue	blue
p-aminodiphenylamine	blue	blue
Phenetole	brown	slight darkening
Dimethyl-p-amino-benzaldehyde	pale yellow	yellow
p-anisidine	violet blue	red
p-dimethylaminophenol oxalate	pink	pink (using ferric alum)
Salicylic acid	violet (after standing overnight)	violet
dl-tryptophane	pink	slight pink in acid solution
β-indolylacetic acid	pink	pink in acid solution
Indole	blue	
β-indolyl-propionic acid	blue	
Dihydroxyphenylalanine	green	pink turning to slate blue on standing
Protocatechuic acid	green	slate blue

TABLE 6

Comparison of the Colour produced on Bentonite by Clover Root Excretions, Dihydroxyphenylalanine, Tryptophane, and β-indolyl Acetic Acid

Sample	*Colour produced on the bentonite*	*Effect of acid on colour*	*Effect of alkali on colour*	*Effect of reducing agents*
Bentonite from clover plants	mainly blue, some pink	increased in intensity	decolorized	no effect
Bentonite plus indolyl acetic acid	pink	increased in intensity	decolorized	no effect
Bentonite plus dihydroxy-phenylalanine	slate-blue	increased in intensity	decolorized	colour disappears
Bentonite plus trypto-phane	pink	increased in intensity	decolorized	no effect

Summary

The reaction leading to the formation of coloured complexes between bentonite and root secretions from clover plants and also between bentonite and certain chemical compounds has been investigated. The results indicate that iron present either in the lattice or as impurity in the bentonite is an important factor in the development of the coloured complexes.

The type of crystal lattice and of the pretreatment of the bentonite on the complex formation with the root secretions from clover plants has also been studied.

Root secretions from several species of plants have been shown to form characteristic coloured complexes with added bentonite.

Attempts have been made to elute the complexes from the bentonite.

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